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A STRATIFICATION OF REMAINS AT AN EARLY MAYA SITE

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The chronology of the Maya civilization of Middle America has been recovered in bare outline by the decipherment of hieroglyphic inscriptions recording a series of dates in the native calendar extending from 98 B.C. (according to the Morley-Spinden correlation) to shortly before the Spanish conquest. Knowledge of the events of Maya history is however extremely scanty, because the textual portions of the inscriptions have so far resisted decipherment, and such native histories as were written after the conquest concern themselves only with the later events of prehistoric times. Solution, therefore, of highly important problems relating to the origin, the growth, and the spread of Maya culture; and its relationship with other advanced cultures of Middle America, must be arrived at largely by archaeological methods.

The study of Maya archaeology has been greatly hampered by the inaccessibility of the early cities, and by the fact that most of them lie buried in tropical jungles so dense that excavation is both difficult and extremely costly. Hence very little digging has been done, and almost no deposits have been found so stratified as to permit the identification of sequences in Maya material culture, particularly in the all-important matter of the development of Maya ceramic types. As potsherds are to the archaeologist what fossils are to the paleontologist, this lack of stratigraphic information as to pottery has for years been an almost insuperable obstacle to progress.

The third season's excavations by the Carnegie Institution at Uaxactun in the department of Peten, Guatemala, have resulted in the finding of very interesting and important stratigraphic conditions. Uaxactun was discovered by Dr. S. G. Morley during the course of the Institution's expedition of 1916. On the basis of the hieroglyphic dates, it appears to have been the oldest and the longest inhabited of the ancient Maya cities. It consists of a series of courtyards or plazas, each one surrounded by great artificial mounds most of them topped by the ruins of temples. One of

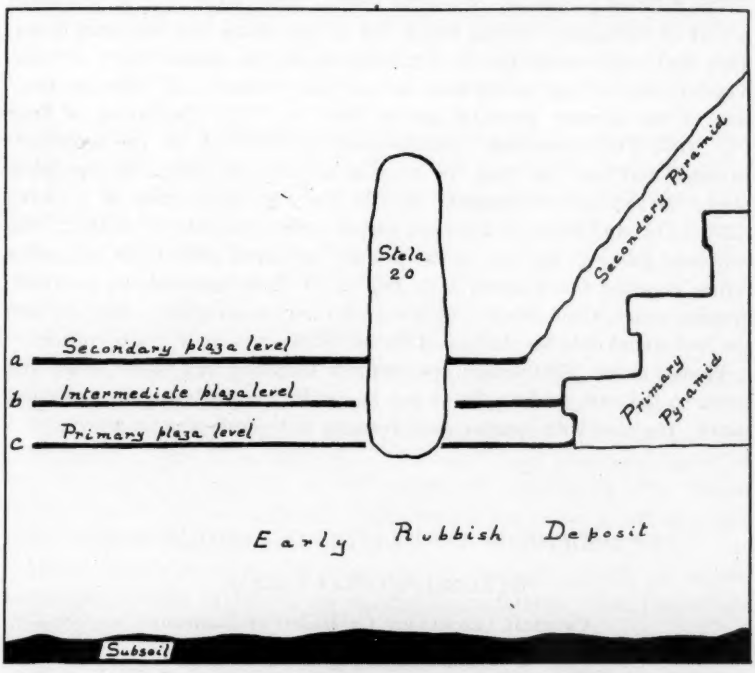
these plazas (Group E) was selected for investigation by the expedition of 1927, because several of the structures enclosing it gave evidence of having been so placed as to serve as markers of certain recurring astronomical phenomena. During 1927 there was cleared a long mound on the east side of the group upon which stood three small temples; toward the end of the season excavation was started upon a high pyramidal mound (E VII) closing in the west side of the plaza. In and in front of this mound were discovered late in 1927 and during the season of 1928 the stratified remains above-mentioned.

The pyramid E VII was built of rough rubble masonry and had presumably been faced with lime stucco. Time and the growth of forest trees had almost completely destroyed its exterior finish, but enough persisted to show that it had been a very steep structure some 50 feet high, with an eastern stairway and a small terminal platform. Close against the east side, at the foot of the stairway, stood a monolithic limestone monument (Stela 20) bearing the Maya date 9.3.0.0.0 (235 A.D. Morley-Spinden correlation). Examination of the plaza showed that a hard-packed lime floor ("*a*," Fig. 1) impinged upon the stela and upon the base of the pyramid. It was obvious therefore that the pyramid had been constructed, the stela erected, and the floor laid during the course of a single building operation, which took place (unless the stela had previously been erected elsewhere) in 9.3.0.0.0. Irrespective of date, however, the floor-stela-pyramid complex surely represents the latest construction at that spot.

In 1927 the work on the pyramid had exposed parts of another smaller pyramid buried beneath it. In 1928 the outer pyramid was removed and the earlier building was exposed. It proved to be a stepped pyramid of stone, 25 feet high, with stairways facing the four cardinal directions. A small platform formed the summit. The entire structure was coated with fine lime stucco, and was ornamented with grotesque stucco masks of colossal proportions. Having been in good repair when it was entombed by the erection of the secondary pyramid, and having been perfectly protected by it through the centuries, the primary pyramid stands today in almost its original condition. It is entirely unlike any known Maya building, but it is, of course, much older than any other Maya building hitherto observed.

After the clearing of the primary pyramid, a pit was dug just east of it in the plaza a few feet north of Stela 20. This part of the work was carried out by Dr. G. C. Vaillant of the American Museum of Natural History, who, at the invitation of the Institution, was visiting Uaxactun as ceramic consultant. The pit was first sunk to undisturbed subsoil and was then enlarged by wing-trenches, one running south to the north side of the stela, the other west to the east face of the primary pyramid. Conditions dis-

closed were extremely interesting. Below the late plaza level ("*a*," Fig. 1) was a second fine, hard floor ("*b*," Fig. 1) which impinged upon the primary pyramid a little above its base; below this was a third similar floor ("*c*," Fig. 1) which joined the base of the pyramid and was evidently constructed at the same time as the pyramid. Both these lower floors had been broken during ancient times in process of digging a large rough hole for the recep-



Conditions at east side of structure E VII (diagrammatic).

tion of the butt of the stela. The stela was therefore erected subsequent to the building of the primary pyramid and floors "*c*" and "*b*."

Between the lowest floor "*c*" and virgin subsoil and extending westward underneath the primary pyramid lay about 4 feet of refuse, rich dark earth containing a few building stones and large numbers of potsherds, whole and broken effigies, and a few animal bones. A much decayed human skeleton was found about 2 feet from bottom. The refuse appears to be typical midden material, lying as originally deposited. The pottery and effigies are of types not hitherto known from the Maya area and are radically different from those taken from the eastern temples (E I, E II, E III) and from the fill of the secondary pyramids.

A second pit was sunk on the east side of the plaza in front of the space between Temples E I and E II and north of Stela 18 (8.16.0.0.0., 97 A.D.). Almost identical conditions were encountered, and floor levels pierced by the stela butt and presumably corresponding to "*b*" and "*c*" of the E VII pit, were observed to run beneath the substructure of the temples, indicating the presence below it of an early buried building.

The following sequence of events may be postulated: (1) A prolonged period of occupancy during which the 4 foot refuse bed was laid down. This took place prior to the development of the classic Maya culture. The buildings of this period have not yet been located. (2) The construction of the primary pyramid and of floor "*c*." (3) The laying of floor "*b*." (4) The apparently simultaneous construction of the secondary pyramid and floor "*a*," and the erection of Stela 20. Stela 20, the latest object in this entire complex, records the very early date of 9.3.0.0.0 (235 A.D.), and Stela 18 the even earlier date 8.16.0.0.0 (97 A.D.). One can only guess at the age of the primary pyramid and of the still older refuse deposits which underlie it, but as all these materials lie in stratigraphic order, their relative ages are certainly established; they furnish the first sound data for studies on the morphology of early Maya culture.

Plans for the 1929 season contemplate following the floors across the plaza to the east, and to the as yet unexplored mounds to the north and south; together with extensive excavations in the sub-plaza rubbish.

THE DEGREE OF ASSOCIATION OF SODIUM VAPOR

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In sodium vapor, the presence of diatomic molecules has long been recognized. Ladenburg and Minkowski[1] have pointed out that their calculation of the chemical constant of sodium is subject to an undeterminable error owing to the presence of sodium molecules. Edmonson and Egerton[2] have suggested that deviations of the observed value from the theoretical value of the chemical constant of sodium might be explained by the presence of diatomic molecules. In the following work a determination of the heat of dissociation of the molecule, Na_2, was made from band spectra observations and from this, by using the theoretical Sackur-Tetrode[3] equation, the degree of association was estimated. The results contradict all previous hypotheses concerning the monatomicity of sodium vapor and indicate that a very large portion of it is diatomic.

In the pursuit of another problem[4] the absorption spectrum of an alloy of sodium and potassium was photographed by Dr. Ritschl and the author. As is well known,[5] this spectrum consists of the green sodium bands, the yellow NaK bands, the red sodium bands, and the far-red potassium bands. An incandescent lamp was used as the light source and a Rowland grating of one meter radius of curvature (dispersion 170 Å/cm. for first order) as the spectrograph. The formula[6] for the heads of the green sodium bands is:

$$\nu = 20{,}298 + (122.6\, n' - 0.61\, n'^2) - (157\, n'' - 0.659\, n''^2)$$

Extrapolating the vibration quants one obtains as the convergence frequency for the excited state $\nu_c' = 26{,}458$ cm.$^{-1}$; for the unexcited state, $\nu''_c = 10{,}941$ cm.$^{-1}$ The heat of dissociation, D may be calculated from these values.[7]

$$D = \nu_c' - A = 9486 \text{ cm.}^{-1} \quad (a)$$
$$= \nu_0 - \nu_c'' = 9357 \quad (b)$$
$$\text{or } 9422 \text{ (average)}$$
$$= 26.8 \text{ cal.}$$

A is the excitation energy $^2S - {}^2P$ for the sodium D line. $\nu_0 = 20{,}298$ in the above formula.

This value is to be compared with the values obtained from the equation of Loomis (loc. cit., $D_a = 8066$; $D_b = 6644$ cm.$^{-1}$) and from the equation of Watson and Fredrickson (loc. cit., $D_a = 8198$; $D_b = 10{,}890$ cm.$^{-1}$). It may be seen that the author's values of D agree within one per cent, which speaks well for the accuracy of his formula.

Using 26.8 cal. as the heat of dissociation of diatomic sodium, the degree of association was calculated for various temperatures. The results are given in table 1.

TABLE 1

TEMP. °C.	PRESSURE MM. HG	DEGREE ASSOCIATION
25	1.1×10^{-11}	0.93 [0.92]
223	4.6×10^{-4}	0.87
400	0.384	0.81
743	186	0.68
880	760	0.62 [0.56]
	(76)	(0.21)
	(7.6)	(0.03)

The pressures given were calculated from the equation of Rodebush and De Vries.[8] They agree with measurements of Edmonson and Egerton[9] and measurements of Haber and Zisch.[10] These values, it is true, were obtained on the assumption that sodium was monatomic. If sodium were diatomic, the recorded vapor pressures obtained from diffusion experiments would be $\sqrt{2}$ times the correct values. The figures in brackets in table 1

are the degrees of association one would obtain for such a case. The correct value of the degree of association probably lies somewhere between the two given in the table. Provided the underlying assumptions are correct, it seems from these calculations that sodium vapor is *mostly diatomic*, especially at the lower temperatures.

A similar calculation has been made by Carrelli and Pringsheim[11] for potassium vapor. They find from fluorescence measurements that $D = 14$ cal.[12] This gives very low values for the degree of association of potassium vapor[13] and does not change any of our notions regarding its monatomic character.

On looking through the literature, it is found that the vapor density of sodium has never been satisfactorily determined because of the high reactivity of sodium toward various containers.[14] Robitsch[15] gives for the ratio of specific heats $C_p/C_v = 1.68 \pm 0.03$. The above results cannot be harmonized with his. It seems also that the experiments of Taylor[16,17] on the magnetic moment of sodium contradict the conclusion that sodium is largely diatomic at the lower temperatures. As the ground state of the Na_2 molecule is a ^1S term, its magnetic moment should be zero and one should obtain in the pattern a central line corresponding to the zero moment of the molecule. No trace of this was found. This inconsistency may perhaps be explained away by saying that the pressure in the sodium boiler was much less than the vapor pressure in equilibrium at that temperature. This is because the boiler was connected directly to the pump (10^{-5} mm.) with only a narrow tube between to reduce the rate of diffusion. Naturally, the degree of *dissociation* would be much greater, the less the pressure.

In all of the work on the vapor pressure, entropy, dispersion, and chemical constant of sodium vapor, the assumption has been made that the vapor is monatomic. That satisfactory results have usually been obtained is due to the fact that the heat of dissociation is so near the heat of vaporization (24.6 cal.). If this were exactly true the degree of dissociation would remain almost constant over the whole temperature range.[17]

[1] *Z. Physik*, **8** (22) 140.

[2] *Proc. Roy. Soc.*, **A113** (27) 538.

[3] *Ann. Physik* [4] **38** (12) 434. Lewis and Randall, *Thermodynamics*, p. 462.

[4] Ritschl and Villars, *Naturwissenschaften*, **16**, 219–20 (1928).

[5] Barratt, *Proc. Roy. Soc.*, **A105**, 221. Pringsheim, *Z. Physik*, **38**, 161.

[6] Cf. Loomis, *Phys. Rev.*, **29**, 607 (1927); **31**, 323 (1928). Frederickson and Watson, *Phys. Rev.*, **30**, 439 (1927).

[7] Franck, *Trans. Faraday Soc.*, **21**, 536 (1925). Witmer, *Proc. Nat. Acad. Sci.*, **12**, 238 (1926). Kuhn, *Z. Physik*, **39**, 77 (1926).

[8] *J. Am. Chem. Soc.*, **47**, 2492 (1925).

[9] *Proc. Roy. Soc.*, **A113**, 526 (1927).

[10] *Z. Physik*, **9**, 302 (1922).

[11] *Z. Physik*, **44**, 643 (1927).

[12] The author measured also the red potassium bands. These were much closer together than the sodium bands and the differences in vibrational energy were of the same order of magnitude as the experimental error of measurement. D_a was 5557 cm.$^{-1}$; D_b was 3240 cm.$^{-1}$ The average value, 4399 cm.$^{-1}$ (12.6 cal.) agrees well, however, with the 14 cal. which Carrelli and Pringsheim estimate.

[13] Cf. Ditchburn (*Proc. Roy. Soc.*, **A117**, 486–508 (1928)) who also estimates the degree of association of potassium vapor and gets results concordant with Pringsheim.

[14] Abegg, *Handbuch II*, **1**, 211 (1908); Dewar and Scott, *Proc. Roy. Soc.*, **29**, 206; 490 (1879); *Chem. News*, **40**, 293 (1879); V. Meyer, *Ber.*, **13**, 391 (1880); Ruff and Johannsen, *Ber.*, **38**, 3601 (1905).

[15] *Ann. Physik*, **38**, 1027 (1912).

[16] *Phys. Rev.*, **28**, 576 (1926).

[17] Professor Rodebush very kindly pointed this out to the author.

THE INTERRELATION BETWEEN DIATOMS, THEIR CHEMICAL ENVIRONMENT, AND UPWELLING WATER IN THE SEA, OFF THE COAST OF SOUTHERN CALIFORNIA

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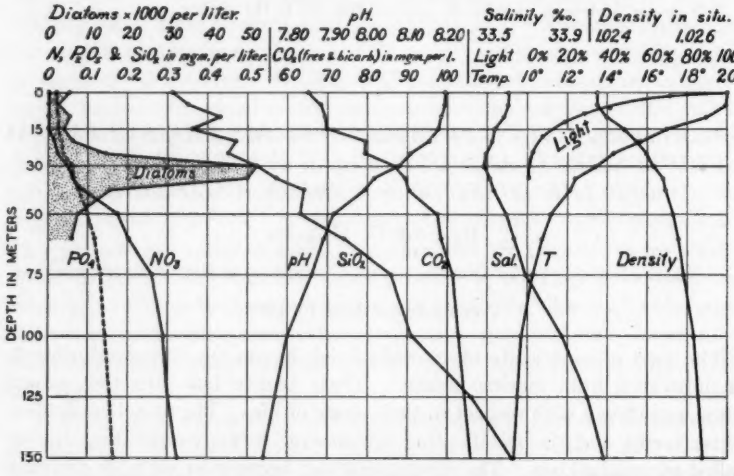
The food of practically all animals living in the sea is derived, directly or indirectly, from marine plants.[1] These plants fall into two groups when considered with respect to their mode of life: The attached shallow-water forms and the free-floating microscopic forms constituting the so-called phytoplankton. The phytoplankton, because of its wide distribution over deep as well as shallow water and because of the large numbers and rapid growth of the organisms composing it, is probably far more important than the other group as regards the synthesis of substances upon which all marine animals ultimately depend. A correlation between the abundance of phytoplankton, which may vary not only with depth and season but with locality and year, and the abundance of animals, including those of commercial importance, is consequently to be expected and efforts to ascertain what factors control the production of phytoplankton are of interest from both a purely scientific and an economic point of view.

For the growth of phytoplankton certain favorable physical conditions and an adequate supply of a number of chemical substances are required. Many of these chemicals occur in sea water in relatively large amounts and are always available to the plants, whereas others are exceedingly scarce and at times may be so small in quantity as to escape detection by the most

sensitive methods. To the latter category belong inorganic nitrogen compounds, phosphates, silicates, and possibly others. These substances, together with carbon dioxide and certain physical factors, probably control the production of plants and, thus indirectly, of animals in the sea.

The Scripps Institution has, for a number of years, been engaged in making quantitative investigations of phytoplankton, physical conditions, and, more recently, of some of the chemical constituents of the water along the coast of Southern California. Most of these investigations have been made on surface water near shore, especially at the Institution pier, but since 1921 intensive studies have been made, during at least six weeks each summer, of both surface and subsurface water from two stations



located five and ten miles seaward from the pier. The depths at these stations are about 350 and 700 meters, respectively.

In the course of these studies it has been found that in this locality the diatoms greatly outnumber any other component of the phytoplankton at all seasons and may therefore be used as an index of photosynthetic activity. The same has been found to be true in most other localities where plankton has been studied and as a consequence more information is available concerning the abundance and ecological relation of diatoms than of any other marine plants. For these reasons only the diatoms are considered in this paper.

The graph illustrating this paper represents the results of studies made during the summer of 1926 at the ten-mile station mentioned above and is intended to show the distribution of the diatoms and the physical and chemical conditions in a column of water and to indicate the relation of

diatoms to various environmental factors. The diatom curve was drawn from figures published by Allen[2] and for each depth indicated shows the average number of cells per liter for sixteen hauls taken between June 3rd and August 21st. The other curves, with the exception of light, represent averages for the same station and the same period as the diatom curve. Unfortunately, no information concerning submarine illumination is available for this locality and the curve shown was constructed from data obtained by Poole and Atkins[3] on October 1, 1925, in the English Channel about 20 miles from Plymouth.

The graph shows that all of the physical and chemical conditions varied greatly with depth and that in nearly all cases most of the variation was confined to a relatively narrow zone, which may be referred to as the transition zone, between the 15- and 50-meter levels. Above this zone the conditions were relatively uniform whereas below they varied at a slow but constant rate.

The graph also shows very pronounced differences in the vertical distribution of the diatoms. They were most numerous at 30 and 35 meters below the surface, i.e., in about the center of the transition zone, where they averaged 50,000 to the liter, whereas at most other depths only about one-tenth as many, or 5000, were found.

Because of this marked accumulation of diatoms in a relatively narrow zone, the environmental conditions as they were found in this zone will be discussed in more detail. Although, due to our imperfect knowledge of the metabolism of diatoms and of many of the environmental factors, definite conclusions are not justified, the data indicate certain relationships and suggest a number of problems which require further investigation, preferably both by laboratory experiments and by field observations.

The graph shows that the diatoms occupied a stratum of water in which the temperature varied according to depth from 10° or less to 20° and that they were most abundant at depths where the temperature averaged about 13° or 7° less than at the surface. The temperature optimum for diatoms is not known but, judging by the relation of temperature to photosynthesis in the case of other plants, it might be supposed that 20° would be more favorable for growth than 13°. In this connection it is of interest to recall that the seasonal distribution of diatoms varies almost inversely as the temperature but the relation is probably not one of cause and effect.

It is realized that the light curve does not necessarily represent the submarine illumination off the coast of Southern California but a number of investigators in various localities have obtained curves essentially similar to the one here shown. According to this curve most of the light was absorbed in the first few meters of water below the surface, only about one per cent of the total daylight reaching a depth of 30 meters. The penetra-

tion of light increases, of course, with decrease in latitude provided other factors, such as turbidity, are constant and it may be assumed that at the station under consideration the amount of light reaching the stratum of greatest diatom content was probably somewhat greater than indicated by the curve. The photosynthetic activity of diatoms at various depths, and therefore at various light intensities, was recently studied by Marshall and Orr[4] by suspending diatom cultures at different levels below the surface. At the latitude of Northern Scotland the maximum amount of photosynthesis occurred at 2 or 3 meters below the surface and above this depth the light was too intense, causing injury to the diatoms. Below the level of optimum illumination photosynthesis gradually diminished until at 20 or 30 meters it was just sufficient to balance respiration. In our latitude an effective amount of photosynthesis would no doubt be possible somewhat below 20 or 30 meters but when it is realized that a dense layer of diatoms, such as was found at 30 and 35 meters, is an effective screen for obstructing the passage of light, it seems very probable that during the summer of 1926 the production of diatoms below 35 meters was limited by insufficient illumination.

In regard to the important chemical substances, carbon dioxide, silica, phosphate, and nitrate, we find that the quantities were in all cases greater in the diatom zone than at the surface. The graph shows only the carbon dioxide existing as bicarbonate, except for small quantities of carbonic acid below 35 meters. Although only half the bicarbonate CO_2 can be utilized by plants it is doubtful if this substance retarded the growth of diatoms since even at the surface the quantity available was about 30 milligrams per liter and it is known that much smaller quantities will support photosynthesis. Silica, also, appears to have been present in sufficient quantities at all levels. Its distribution differed from that of the other substances in that the increase in quantity with depth was at a nearly uniform rate throughout the entire column of water represented by the graph. This was probably due to gradual dissolving of the tests of sinking dead diatoms. Phosphate was, on the average, less abundant than any other substance determined, although it was not completely lacking at any depth, the quantity at the surface being 0.02 milligram per liter. It is known that even smaller amounts can be utilized by diatoms since Atkins[5] has found that during periods of rapid diatom growth phosphate may be completely removed from the surface water of the English Channel. At the station represented by the graph the cause of the low diatom content in the upper 25 meters of water was consequently not an insufficient supply of phosphate. The increase in quantity with depth was shown most strikingly by the nitrate. Above 20 meters this substance was entirely lacking, or at least could not be detected with a reagent which is sensitive to quantities as small as 0.002 milligram per liter of nitrate

and nitrite nitrogen. Below 25 meters nitrate increased rapidly and the rate of increase in the transition zone was more pronounced than for other substances. A causal relation between the abundance of diatoms and the quantity of nitrate is thus strongly indicated and, assuming that no other source of nitrogen, for example ammonia, was available, it can be stated that lack of nitrogen prevented a greater production of diatoms in the upper 25 meters of water.

The effect of various hydrogen-ion concentrations upon the growth of diatoms has not been investigated, but, since growth processes of some plants appear to be affected by changes in the hydrogen-ion content of the external medium, it is of interest to note that in the photosynthetic zone the variability of pH was the greatest.

Other properties of sea water which require consideration when attempting to explain the distribution of organisms in a vertical column of water are density and viscosity. These are not directly concerned with growth but are practically the only external factors affecting the floating power of organisms. According to the graph, density increased rapidly with depth between 5 and 35 meters and more gradually at greater depths. A curve for viscosity is not shown but it can be stated that it would be practically the reverse of the temperature curve since viscosity is but slightly affected by variations in salinity. At 35 meters the water was about one-fifth more viscous than at the surface and hence resisted the vertical movement of organisms to a corresponding extent. Some investigators maintain, for reasons that cannot be discussed here, that organisms are independent of, or can adjust themselves to, changes within a certain range of the density and viscosity of the medium in which they live but it is at least possible that the majority of the diatoms here dealt with were unable to maintain their position except in the water of intermediate density and viscosity occurring at 30 and 35 meters.

To summarize, the data presented above show that during the summer of 1926, the diatoms in the area studied were confined chiefly to a relatively narrow zone at 30 and 35 meters below the surface. The data also suggest that an extensive development of diatoms was possible only in this zone, since at the higher levels the water was deficient in nitrate and at lower levels, where there was an abundant supply of all the materials required for plant growth, the illumination was inadequate. It cannot be stated however whether the vertical position of the diatoms was determined by factors directly concerned with growth, by purely physical factors, or by a combination of the two types.

Under conditions such as those summarized in the preceding paragraph, and assuming that there is no vertical movement of water, heat from the sun, aided by wind action, will lower the thermocline until a stratum of water of uniform physical conditions will extend well below the present

diatom zone. The temperature of this water will be high and the density and viscosity low. If the diatoms are unable to float in this water they will sink to depths where light is insufficient for photosynthesis but if they are independent of density and viscosity the supply of one or more of the chemical substances will ultimately be exhausted at all levels where light is sufficient for photosynthesis. In either case further diatom production will be impossible until more favorable physical and chemical conditions are reëstablished.

In any locality the restoration of chemicals may be accomplished by one or more of the following agencies: By run-off from land, by decomposition of organic material, or by influx of water from other localities and depths. In a region of slight rain-fall, such as Southern California, run-off from land is probably a negligible factor and it has been found that decomposition takes place chiefly at or near the bottom. It may be concluded therefore that in this locality water from the deeper layers is the principal agency supplying nutrient salts to the photosynthetic zone. The same agency, as well as cooling of the surface water due to seasonal changes, will also alter the physical conditions of the water near the surface.

There are three quite distinct ways in which subsurface water may be elevated. One is simply a mechanical mixing of water of uniform density and is caused by wind action. This mixing is of great importance in the higher latitudes where the temperature and density gradients are eliminated when the surface water cools in the fall.[6] In the latitude of Southern California these gradients are never entirely eliminated, although considerably reduced during the winter. Consequently, mixing extends below the photosynthetic zone during a relatively short period only and, except in very shallow water, never to the bottom. McEwen calls attention to another type of turbulence which he describes as follows:[7] ". . . .heat is removed from the water surface by evaporation, back radiation, and conduction through the air. The resulting increase in specific gravity of a thin surface layer of the water causes a settling of relatively heavy and cool masses of surface water, compensated by a rise of relatively warm and lighter water." When the gradients are as pronounced as shown by the graph the transfer of water due to this circulation is probably negligible below a few meters from the surface.

The third type of vertical circulation, commonly known as upwelling, consists of a more or less continuous upward movement of bottom water and is characteristic of certain areas along the western shores of the African and American continents. The existence of this phenomenon along the coast of Southern California has been demonstrated by McEwen[8] who found that the rate of upwelling varies with the season and locality. He also showed that temperature reduction, i.e., the difference between

the observed and the normal temperature for the latitude and season, can be used as an index of the rate of upwelling.

The relation of upwelling to the production of organisms in this region was pointed out by Michael[9] who found indications of a positive correlation between temperature reduction and quantity of plankton. The probability of the existence of such a relation is greatly strengthened by the data presented in this paper. The graph clearly shows that an upward movement of water will result not only in a reduction of the temperature but in an increase of density, viscosity and chemical substances in the photosynthetic zone, i.e., all the environmental conditions, with the exception of light, will be affected. The magnitude of the effect will, of course, be proportional to the rate of upwelling and the exact manner in which the diatoms are affected depends to a certain extent upon their relation to density and viscosity.

Referring again to a situation similar to that represented by the graph, a certain amount of upwelling is required to maintain the existing conditions, or to replace the water heated by the sun and depleted of nutrient substances by the plants. If the rate of upwelling is too slow to maintain equilibrium, conditions similar to those resulting from stationary water will be established, although with some delay. On the other hand, if water is moving toward the surface at a speed greater than necessary to counteract the changes caused by the sun and the diatoms, the heavier water, together with its load of chemicals, will be carried past the diatom zone and possibly to the surface. This will make photosynthesis nearer the surface possible and will enable the diatoms, provided they are able to float in water of any density, to occupy a wider stratum of water, the upper limit of which will be determined by excessive illumination and the lower by insufficient illumination. In the case represented by the graph the upper limit of the diatom zone would thus be raised from about 30 to about 5 meters below the surface. The width of the diatom zone would probably not be increased to a corresponding extent since, if the total number of diatoms is augmented, more light will be absorbed and perhaps become inadequate for photosynthesis before reaching the 35-meter level. If the distribution of diatoms is controlled also by density and viscosity, rapid upwelling will not necessarily widen the diatom zone but will bring it nearer the surface where light conditions are more favorable.

[1] In this article all photosynthetic organisms are considered as plants.

[2] Allen, W. E., *Bull. Scripps Inst. Oceanog. Tech. Ser.*, **1**, 201 (1928).

[3] Poole, H. H., and W. R. G. Atkins, *J. Mar. Biol. Assoc.*, **14**, 177 (1926).

[4] Marshall, S. M., and A. P. Orr, *Ibid.*, **15**, 321 (1928).

[5] Atkins, W. R. G., *Ibid.*, **15**, 191 (1928).

[6] See, for example, Atkins, W. R. G., *J. Cons. Internat. Explor. de la Mer*, **1**, 197 (1926).

[7] McEwen, G. F., ms.
[8] McEwen, G. F., *Int. Rev. Hydrobiol. u. Hydrog.*, **5**, 243 (1912).
[9] Michael, E. L., Spec. Publ. Bernice P. Bishop Museum No. 7, 555 (1921).

TRANSFORMATION OF CONJUGATE ELEMENTS OR OF CONJUGATE SUBGROUPS

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Every complete set of conjugate elements, or of conjugate subgroups, of a given group G is transformed under G according to a transitive substitution group S. Let G_1 and G_2 belong to such a set and let their normalizers be represented by G_1' and G_2', respectively. If the elements of G are represented in a rectangular form in which the first row is G_1' and the other elements are multiplied on the left by those of G_1' then the elements of G_2' cannot appear in every row since the elements of each row transform G_1 into the same element, or into the same subgroup, and the rows in which elements of G_2' appear cannot transform G_1 into G_2 since some of them transform G_2 into itself. If the elements of G_2' appear in all except one of the rows then G_2' must transform G_1 into all of its conjugates under G except G_2, and vice versa. Hence, it results that *a necessary and sufficient condition that the constituents of a complete set of conjugates under G are transformed according to a multiply transitive group is that when the elements of G are written in a rectangular form in which the normalizer of one of these conjugates is the first row then the elements of a normalizer of another of them will appear in all except one of these rows.* If the elements of one such normalizer appear in all except one of the rows then the elements of every one of the normalizers of the conjugates of G_1, except the normalizer of G_1, must appear in all except one of these rows, and no two of these normalizers are omitted by the same row.

A necessary and sufficient condition that a complete set of conjugates of G_1 is transformed under G according to an imprimitive group is that the normalizer of one of the set is a non-maximal subgroup of G, and if the normalizer of one of the set is non-maximal then the normalizer of every one of them must have the same property. Hence, it results that two necessary and sufficient conditions that such a set is transformed according to a simply transitive primitive group are that the normalizer of one of the set is a maximal subgroup of G and if such a normalizer constitutes the first row when G is represented in a rectangular form as noted above then at least two of the rows will involve no element of the same other such nor-

malizer. It is, however, not necessary that the elements of these other normalizers appear separately in the same number of rows, as may be seen from the developments which follow.

If the elements of G are written in a rectangular form in which the first row is composed of the elements of G_1', then the elements of G_2' will appear in a number of these rows which is equal to the degree of a transitive constituent in the subgroup S_1 composed of all the substitutions of S which omit a given letter. This number is independent of whether the elements of G are multiplied on the right or on the left by those of G_1' in the given rectangular form, since it is equal to the square of the order of G_1' divided by the order of the cross-cut of G_1' and G_2'. In particular, a necessary and sufficient condition that G transforms the conjugates of G_1 according to a regular group is that all the normalizers of these conjugates coincide with G_1'. Since the co-sets of a group are transformed as units by every operator of the group under which the subgroup with respect to which the co-sets are formed is invariant it results that G_1' transforms the rows of the given rectangle as units according to the substitutions of S_1. Hence, the following theorem: *If a group G which contains a complete set of k conjugates is represented in a rectangular form with respect to the normalizer of one of these conjugates then the numbers of rows in which the normalizers of these conjugates appear separately represent the degrees of the transitive constituents of the subgroup composed of all the substitutions which omit one letter of the transitive group of degree k according to which these conjugates are transformed under G.*

The preceding theorem constitutes a wide generalization of the well-known theorem that the index of the cross-cut of two conjugate subgroups under one of them is always less than the common index of these subgroups taken separately under the entire group.[1] In fact, the latter index is equal to the product of the degree of the transitive group according to which the set of conjugates to which these subgroups belong is transformed under the entire group and the index of one of these conjugates under its normalizer, while the former divides the product of the same index and the degree of a transitive constituent of the subgroup composed of all the substitutions which omit one letter of this transitive group. As the latter degree is at least one less than the former the theorem noted at the close of the preceding paragraph furnishes not only a generalization of the fundamental theorem in question but it also provides an interpretation of its limitations. Two necessary and sufficient conditions that the difference between the given indexes is unity are that the conjugate subgroups coincide with their normalizer and are transformed according to a multiply transitive group under G.

Among the conjugate subgroups of a substitution group G those which are composed of all the substitutions of G which omit a given letter are of

special interest. Let G_1 represent one such subgroup and suppose that the degree of G is n, while the number of its transitive constituents is k. It will be convenient to think of G_1 as having as many conjugates under G as the degree of the transitive constituent of G which involves the letter omitted by all the substitutions of G_1. Two conjugates of G need therefore not be distinct. If a substitution s of G_1 omits l letters of G it appears in l of the n subgroups composed of all the substitutions which omit a given letter of G. Hence, such a substitution is counted l times if the omitted letters in all of these subgroups are counted and the number of letters omitted in all these substitutions is l^2. Since the number of letters omitted in all the substitutions of G is kg, g being the order of G, the number of letters omitted by all the substitutions of the conjugates of G_1 is g times the number of transitive constituents of G when it is regarded as a group of degree n. This constitutes a proof of the following theorem: *The sum of the squares of the letters omitted by all the substitutions of any substitution group G which has k transitive constituents is equal to the product of the order of G and the sum of the transitive constituents in the set of k subgroups obtained by taking successively all the substitutions of G which omit one letter of each of its transitive constituents.*

[1] G. A. Miller, *Annals Math.*, **14**, 95 (1912–13).

OBSERVATIONS UPON COMPLEMENT FIXATION IN INFECTIONS WITH ENDAMOEBA HISTOLYTICA

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The biological activities of *Endamoeba histolytica*, the cause of amoebic dysentery, have always been of much interest to the medical zoölogist, owing to the importance of this parasite as a pathogenic organism in man and to the very marked lesions which are produced by it in the tissues of the human host. It has long been known that it possessed the property of phagocyting the red blood corpuscles of man and of other animals and of penetrating the tissues of the intestine and producing necrosis, with the formation of abscesses and ulcerations. This parasite has also been found in other parts of the human body where it produces abscesses of peculiar character, and in experimental animals, as the cat and dog, similar pathological lesions have been produced experimentally, by numerous observers.

Owing to the fact that cultures of *Endamoeba histolytica* were not available until quite recently, it was not possible to more than theorize upon the manner in which this parasite produced the lesions invariably associated with its presence in the tissue, but the successful cultivation of the organism by Boeck and Drbohlav[1] and others, has made possible more accurate observations regarding this subject and also observations upon the reaction of the human host to invasion by the parasite.

In 1927, the writer[2] demonstrated hemolytic and cytolytic substances in alcoholic extracts of cultures of *Endamoeba histolytica*. While the conception that the pathogenic effects of this parasite upon the tissues of man and experimental animals were due to a toxin, or toxins, cytolytic in nature, secreted by the organism, it was not until this demonstration that it was shown experimentally that such agents did exist in the parasite, and this demonstration was only rendered possible by the possibility of the cultivation of the organism. The work referred to demonstrated that in alcoholic extracts of forty-eight hour old cultures of *Endamoeba histolytica*, grown upon the Locke-egg-serum medium of Boeck and Drbohlav or the Locke-serum medium of the writer,[3] there is present a hemolysin capable of dissolving the red blood corpuscles of man, rabbits and guinea-pigs. This hemolysin was destroyed by heating the extracts for one hour in a water bath at 80°C. and was practically insoluble in normal salt solution but soluble in absolute alcohol. It was not an exotoxin, as it was not present in the fluid portion of the cultures or in extracts of cultures over forty-eight hours old. That the hemolysin was intimately connected with the living amoebae was shown by the fact that extracts of cultures containing only dead amoebae were inert so far as hemolysis was concerned.

The extracts of cultures of *Endamoeba histolytica* also contained a cytolysin capable of dissolving the epithelial cells of the mucous membrane of the intestine, but neither the cytolysin nor the hemolysin were specific for the cells of man, the cytolysin dissolving the intestinal epithelial cells of the mucous membrane of man and of the cat, while the hemolysin dissolved the red blood corpuscles of man, rabbits and guinea-pigs. Bacteriolytic substances could not be demonstrated, this being in accordance with the well-known fact that *Endamoeba histolytica* does not ingest bacteria under normal conditions in man although it does ingest the red blood corpuscles and intestinal epithelial cells of its host.

The observation just mentioned, while of much interest from the standpoint of the etiology of the pathogenic lesions characteristic of invasion of the tissues of man and experimental animals by *Endamoeba histolytica*, are not of as great theoretical and practical importance as the fact that these alcoholic extracts of the cultures of this parasite, when used as antigens in a complement fixation test, have been found to be of value in the diagnosis of infections with the organism. Thus, it has been found that the

blood serum of individuals infected with *Endamoeba histolytica* contains antibodies which, in the presence of alcoholic extracts of the cultures of the parasite, fix complement, and that this reaction is apparently specific.

Technique.—The antigens used in the complement fixation tests were prepared by extracting with from seven to ten parts of absolute alcohol, the sediment of from sixty to eighty cultures of *Endamoeba histolytica* grown upon the Locke-egg-serum medium of Boeck and Drbohlav for forty-eight hours, as the sediment of such cultures contains practically all of the amoebae. The cultures were extracted in the incubator at 37°C. for ten days, the mixture being thoroughly shaken several times a day during that period. After extraction the mixture was filtered and the filtrate used as an antigen in the tests.

As a control, extracts were prepared in the same manner from cultures upon the same medium of all of the bacteria growing with the amoebae. In no instance did these bacterial antigens give a positive reaction when used as a control.

The technique of the complement fixation test was the same as that used as the standard method for performing the complement fixation test for syphilis in the United States Army, and which is fully described in the writer's book entitled "The Wassermann Test." A human hemolytic system was used in the tests, the blood sera tested were inactivated by heating at 56°C. for one-half hour in the water bath, and the sera tested were taken at random from specimens submitted to the serological laboratory of the Army Medical School for the complement fixation test for syphilis. The antigenic extracts were used undiluted, as they were found so weak in complement fixing power that dilution rendered them inert.

After testing the sera, a specimen of feces was requested from each patient tested, whether the result was positive or negative, and this was examined microscopically, culturally, and by sedimentation for *Endamoeba histolytica*. Thus all of the results reported in this contribution have been checked by such examination of the feces of the individual supplying the blood serum tested.

Results of the Complement Fixation Test.—At the time this communication was written three hundred and five blood sera from as many individuals had been tested, of whom 30 gave a positive reaction for *Endamoeba histolytica*, or 9.8 per cent, and 275 sera from as many individuals gave a negative reaction, or 90.1 per cent. Of the 30 positive cases, 26 gave a four-plus reaction (absolute inhibition of hemolysis), while 4 gave a three-plus reaction (less than fifty per cent of hemolysis). There were numerous doubtful reactions but these always cleared up after an hour or two in the ice-box.

Of the 30 positive cases, a check of the feces for *Endamoeba histolytica* resulted in the demonstration of the parasite in 28, or 93.3 per cent.

In two cases, or 6.6 per cent, we were unable to demonstrate this organism in the feces. In one of these cases *Endamoeba coli* was present in the feces.

Of the 30 positive cases, 6 were mixed infections with *Endamoeba histolytica* and *Endamoeba coli*, 2 with *Endamoeba histolytica* and *Endamoeba nana*, and one with *Endamoeba histolytica* and *Chilomastix mesnili*.

Clinically, over 60 per cent of the individuals giving a positive reaction presented symptoms that were probably caused by the parasite, while in the remainder, if any symptoms were present they had not been noted by the patients. In other words, these individuals were so-called "healthy carriers" of *Endamoeba histolytica*.

In the patients presenting symptoms of the infection proper treatment resulted in the disappearance of the positive reaction in all of the cases tested one month after the conclusion of treatment, eight in number. The remaining 22 positive cases were not tested, owing to discharge from the hospital before that period of time had elapsed, or because treatment was not given for the infection.

Of the 275 individuals whose blood sera gave a negative reaction with this test, an examination of the feces resulted in the discovery of but three infections with *Endamoeba histolytica*, or slightly over one per cent.

Among the 275 negative individuals there were 34 infestations with *Endamoeba coli*, 22 with *Endamoeba nana*, 3 with *Iodamoeba williamsi*, 10 with *Chilomastix mesnili*, 7 with *Tirchomonas hominis*, and 2 with *Giardia intestinalis*. There were 11 mixed infestations with *Endamoeba coli* and *Endamoeba nana*, 4 with *Endamoeba coli* and *Chilomastix mesnili*, 2 with *Endamoeba coli* and *Giardia intestinalis*, and one with *Endamoeba coli* and *Trichomonas hominis*.

From the results enumerated it is evident that infestation with intestinal protozoa other than *Endamoeba histolytica* does not cause a positive complement fixation reaction in blood sera with the antigens used in this series of experiments.

Clinically, the individuals who gave a negative reaction were suffering from a wide range of disease conditions, so that it is safe to say that other disease conditions do not give a positive reaction, so far as these experiments demonstrate. In one case of amoebic abscess of the liver, in whom the parasite was very scarce in the feces, a negative reaction was obtained, and it is possible that this result was due to the mild intestinal infection present. Another case of amoebic abscess of the liver gave a strong plus positive complement fixation test and in this individual the feces contained very numerous amoebae of this species.

Relation to Wassermann and Kahn Tests.—Owing to the fact that the antigens used in these tests were not prepared from pure cultures of *Endamoeba histolytica* (as such are not obtainable), and contained extractives not only from the amoebae present but also from the bacteria growing

in the cultures and from the culture medium, it was thought that perhaps the positive results obtained might be due to non-specific substances, as in the antigens used in the Wassermann and Kahn tests for syphilis, in which non-specific substances in the tissues extracted are capable of fixing complement when added to the blood serum of syphilitics. In order to test the theory that the positive results might be due to syphilis a check of the sera tested in these experiments was made and it was found that only one of the 30 positive cases gave a positive Wassermann and Kahn test, while of the 275 negative cases 8 gave a four-plus Wassermann reaction and 11 a four-plus Kahn reaction. It was thus evident that the positive results obtained with the antigens prepared from cultures of *Endamoeba histolytica* were specific in nature and bore no relation to the results obtained with either the Wassermann or Kahn tests.

Discussion of Results.—The results of these experiments in complement fixation with extracts of cultures of *Endamoeba histolytica* demonstrate for the first time, in man, the presence of specific antibodies in the blood serum of individuals infected with this parasite. The exact nature of these bodies is unknown but it is evident that the complement fixation reaction with the antigens described belongs to that very interesting group of reactions in which specific results are obtained with alcoholic extracts and which must depend, so far as we know, upon specific lipoids in the extracts which react with specific lipotropic substances in the blood serum of the infected individual. As long ago as 1915 the writer[4] demonstrated that alcoholic extracts of *Mycobacterium tuberculosis* fixed complement when used as antigens with the blood serum of tubercular individuals, and this observation has since been confirmed by Dienes and Scheff,[5] Lewis,[6] and Furth and Aronson,[7] who have demonstrated that there is a distinct substance in this bacterium which fixes complement when used as an antigen with the blood serum of tubercular patients and which is soluble in alcohol. Similar alcohol-soluble specific substances have been demonstrated in the diphtheria bacillus and Strepthrix by Freund;[8] in *Treponema pallidum* by Craig and Nichols;[9] and in the cercaria of Bilharzia by Fairley.[10] Recently, Kurt Meyer[11] has shown that antisera obtained by injecting rabbits with watery extracts of tapeworms will fix complement in the presence of alcoholic extracts of the worms, and Sachs, Klopstock and Wile[11] have demonstrated that rabbits, when injected with alcoholic extracts of rabbit kidney and pigs serum will develop an antibody to their own tissue lipoids.

It is probable that the substance, or substances, in the alcoholic extracts of *Endamoeba histolytica* used in these experiments, are similar to these bodies and it will be possible, when pure cultures of this organism are obtained, to determine whether specific antibodies are formed in the blood of man in response to injections of alcoholic extracts of such cultures.

The practical value of this complement fixation test in the diagnosis of infection with *Endamoeba histolytica* is still undetermined and is limited by the difficulty of making the antigen and the small amounts obtainable. Some extracts are inert while others give apparently excellent results although prepared in the same manner. Clinically, and as checked by the results of feces examinations, the test would appear to possess a high degree of specificity, and in our hands has proved its value repeatedly in discovering infections which would otherwise have been overlooked. However, our experience has been that practically all individuals giving a positive complement fixation result also showed *Endamoeba histolytica* in their feces, so that the diagnosis could have been made by a fecal examination. When placed upon a clinical basis the test would possess great value if it were used routinely, in that it would pick up many infections which are latent and in which a fecal examination would not be considered as necessary, owing to the absence of clinical symptoms. At the present time the test is not on a practical basis but efforts are being made to secure a more efficient antigen by other methods of extraction of the cultures.

Conclusions.—The following conclusions appear to be justified by the results of the experiments detailed in this communication:

1. There occur in the blood serum of individuals infected with *Endamoeba histolytica* specific immune substances which can be demonstrated by complement fixation when alcoholic extracts of cultures of this parasite are employed as antigens.

2. These complement fixing bodies disappear from the blood serum after treatment resulting in the disappearance of *Endamoeba histolytica* from the feces of the individual.

3. Individuals free from infection with *Endamoeba histolytica* do not give a positive complement fixation reaction with the alcoholic extracts of cultures of *Endamoeba histolytica*, nor do those infested with *Endamoeba coli*, *Endamoeba nana*, *Iodamoeba williamsi*, *Chilomastix mesnili*, *Trichomonas hominis*, or *Giardia intestinalis*.

4. The reaction does not occur in individuals suffering from other infestions or diseases.

5. The reaction does not occur in individuals giving a positive Wassermann or Kahn test unless infection with *Endamoeba histolytica* is present.

6. Positive complement fixation reactions occur with these antigens in individuals suffering from symptoms of infection with *Endamoeba histolytica* and also in those in whom symptoms are absent, i.e., in the so-called "healthy carrier" of the parasite.

[1] Boeck, W. C., and Drbohlav, *Amer. Jour. Hyg.*, **5**, 371 (1925).
[2] Craig, Charles F., *Amer. Jour. Trop. Med.*, **7**, 225 (1927).
[3] Craig, Charles F., *Ibid.*, **6**, 333 (1926).
[4] Craig, Charles F., *Amer. Jour. Med. Sci.*, **150**, 781 (1915).

[5] Dienes, L., and Scheff, *Jour. Immunol.*, **12**, 123 (1926).
[6] Lewis, P. A., *Jour. Exper. Med.*, **65** (1927).
[7] Furth, J., and Aronson, *Jour. Immunol.*, **13** (1927).
[8] Freund, J., *Ibid.*, **13**, 79 (1927).
[9] Craig, Charles F., and Nichols, *Jour. Exper. Med.*, **16**, 336 (1912).
[10] Fairley, N. H., *Jour. Path. and Bacter.*, **30**, 1 (1927).
[11] Meyer, Kurt (quoted by Browning, C. H.), *Brit. Med. Jour.*, No. **3490**, November 26, 1927, p. 978. Also Sachs, Klopstock, and Wile (quoted by Browning), *Ibid.*

REVERSIBLE CRYSTALLIZATION IN TENDONS AND ITS FUNCTIONAL SIGNIFICANCE

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Introduction.—Doubly refracting material is of very widespread occurrence in the animal body. This indicates either a high degree of orientation in the molecules and colloidal micellae, or the presence of oriented swarms of minute crystals. A colloidal solution of gold or silver may show no double refraction, although composed of a multitude of small crystals, but if these crystallites are lined up in an electrical field double refraction occurs. In the body many mechanical and electrical forces tend to orient the colloids and they accordingly often show double refraction whether the micellae of which they are composed are molecules or crystallites.

The doubly refracting substances in the body are both inorganic and organic. The inorganic crystals present are almost always calcite or aragonite, two forms of crystalline calcium carbonate. The shells of molluscs, eggshells, the spicules of sponges, the spines of sea urchins, pearl, and coral contain either calcite or aragonite and give x-ray diagrams characteristic of a microcrystalline condition. Bones and dental enamel also contain calcium salts in crystalline form and the x-ray diagrams from bones show characteristic changes with age and pathological condition.[1]

Many organic substances also show very marked anisotropy. Spun fibres such as silk, cocoons and cobwebs are composed of crystalline micellae. The forces involved in secretion align the micellae which crystallize after secretion. These fibres, as well as natural cellulose fibres and some types of rayon, show x-ray diagrams indicating a regular arrangement of crystallites with respect to the fibre axis, and the more perfect the fibre pattern the greater the strength and durability of the fibre.

In the animal body chitin, collagen, elastin, spongin, fibrin and the muscle proteins show a double refraction which indicates an alignment of the

colloidal micellae. Whether these micellae are crystalline or not may depend on their temperature, acidity and state of hydration. As their appearance under crossed nicols is the same whether they are in liquid crystal or solid crystal condition evidence on this point can only be obtained from x-ray diffraction patterns.

Significance of X-Ray Diffraction Patterns.—The apparatus used to obtain pin-hole diffraction patterns was described in a previous article.[2] A narrow beam of monochromatic x-rays from a molybdenum tube, after

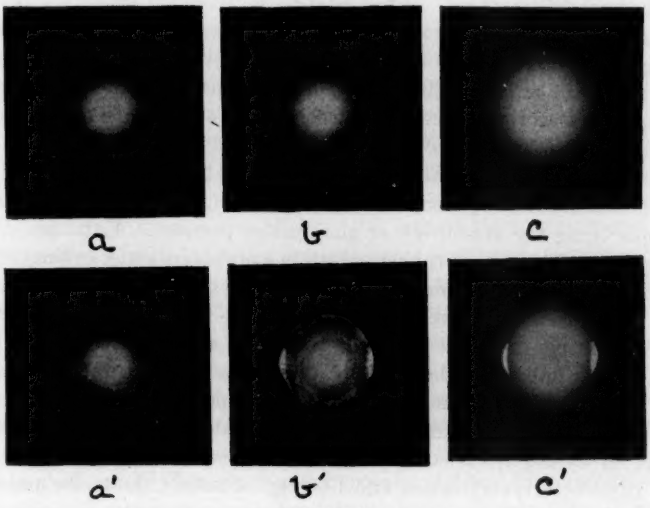

FIGURE 1

X-ray diffraction patterns from white fibrous tissue (tendon from forearm of dog); (*a*) fresh, moist, unstretched, 2nd order zone with 3rd order zone faintly visible, (*b*) fresh, moist, stretched, arcs on edge of 2nd order zone in direction of stretching, (*c*) stretched and dried, arcs left but no zones. As the untouched photographs do not reproduce well *a' b' c'* are also given which are prints from the same negatives as *a*, *b*, *c*, with the arcs and zones intensified.

passing through two pin-holes in sheets of lead, falls on the specimen under observation, and produces a diffraction pattern on a photographic plate placed a short distance beyond the specimen. It takes an exposure of about 25 milliampere hours to give a photograph. With this monochromatic pin-hole method a single crystal in which the molecules are linked in a space lattice gives a Laue pattern of isolated spots. A crystal powder or a microcrystalline structure gives a series of sharp rings. If these microcrystals are aligned with their long axes in one direction the rings break up into spots giving what is known as a fibre pattern. If no true

crystals are present, but if the substance examined is in a liquid crystal condition with the molecules or micellae lined up, thus approaching a crystalline condition, the x-ray diagrams show broad, hazy rings or zones. These are due to first, second, etc., orders of reflection from the boundaries of the aligned molecules or micellae and give a measure of the distance of nearest approach of the molecules as they lie side by side or end to end. If r is the radius of the diffraction ring on the photographic plate and D the distance of the specimen from the plate then r equals $D \tan 2\theta$, where θ is the angle of reflection. When θ has been calculated from this formula then d the distance between the molecular planes can be calculated from Bragg's formula $n\lambda = 2d \sin \theta$, where λ is the wave-length of the x-rays used and n the order of reflection. Diffraction patterns, therefore, furnish a means of measuring molecular dimensions and at the same time of determining whether crystals are present or not.

Changes from Non-Crystal to Crystal Form.—It has long been known that amorphous matter may become doubly refracting under strain, a familiar example being the anisotropy of glass under pressure. Katz[3] and G. L. Clark[1,4] have shown that rubber, which is amorphous under ordinary conditions, gives a typical fibre pattern, indicating the presence of microcrystals, when stretched more than 75 per cent. Gelatin[1,4] gives only an amorphous ring, except at the isoelectric point, where there is in addition a sharp ring indicating the presence of microcrystals in unoriented condition. This is important as it indicates the possibility of gels and colloids passing abruptly from liquid crystal to solid crystal form with a slight change in hydrogen-ion concentration. Gelatin, when stretched, shows more complete crystallization and fibering. Shellac[4] shows the presence of crystals which disappear on polymerization so that the appearance of crystals may accompany depolymerization.

Researches on fluid crystals have shown that they pass abruptly into solid crystal form when they pass a certain critical temperature. The observations given above indicate that gels and colloidal solutions may pass from liquid crystal to solid crystal form, when held at the same temperature, through changes in acidity, tension, state of polymerization or hydration.

The fact that organic gels and colloids may be subject to abrupt changes of state indicates that these changes may have great functional significance. The change in surface forces that would accompany a change in state from a liquid-liquid to a liquid-solid system may be responsible for changes in elasticity, contractility and cohesion. In this paper the x-ray diffraction patterns from white fibrous and yellow elastic tissue were obtained under various conditions in order to see what relation exists between the presence of crystallites in the tissue and its physical properties of elasticity and cohesion.

Tendons.—White, fibrous tissue is largely composed of doubly refracting

collagen fibres bound together with a certain amount of interfibrillar material. Stretching and drying both increase the double refraction of the fibres. On swelling in weak acid or alkali the double refraction is lost but reappears on neutralization. Experiments on elastic fibres show that they lose their fibre form on treatment with weak acid or alkali but if they are neutralized under tension the fibre form reappears. It seems therefore that the double refraction of fibrous and elastic tissue is conditioned by tension and hydrogen-ion concentration.

Evidence so far, in regard to the appearance of true crystals in tendons, is incomplete. Clark[1,4] gives results on isoelectric gelatin which may be closely similar to the collagen of white, fibrous tissue. Isoelectric gelatin, unstretched, has a broad amorphous ring corresponding to a spacing of 4.2 A.U. and a sharp crystalline ring corresponding to a spacing of 2.8 A.U. At 50 per cent elongation the sharp circle becomes two crescents, in the stretching direction, showing orientation or fibering of the crystals. At 100 per cent elongation intensity maxima appear on the inner side of the amorphous ring and also close to the central beam corresponding to spacings of 5.5 and 10 A.U., respectively. Katz and Gerngross[5] give spacings of 2.7, 4.0 and 10.0 A.U. for stretched gelatin and state that they got the same result for collagen, using dried unstretched tendons. Herzog and Gonell[6] give a spacing of 12.1 A.U. for collagen from scales, cartilage, rat tail tendon and the ligamentum nuchae of cattle. In every case the tendons were dried and in some cases treated with trypsin before drying. In this investigation x-ray diffraction patterns were obtained from tendons that were placed in a small, moist chamber immediately after excision, both in a relaxed condition and under tension, and also from tendons dried normally and under tension. Tendons of white, fibrous tissue from the forearm of a dog were used as a source of collagen and the ligamentum nuchae from both dogs and sheep as a source of elastin. The results obtained are given in tables 1 and 2 and diffraction patterns from collagen are shown in figure 1.

Fish scales, nails and moist skin all showed one zone giving a spacing of 6.0–6.2 A.U., if it were a second order, and 3.0–3.1 A.U. if it were a first-order reflection. This corresponds to the spacings found for tendon collagen. Owing to variations in the size and position of the specimen used the measurement of the distance D is not absolutely accurate. Also the haziness of the zones and the width of the arcs made the measurements of the diameters uncertain so that the figures given for the spacings are only approximately correct.

Discussion.—The results given above indicate that collagen exists normally in skin and tendons in a liquid crystal condition with the molecules aligned in such a regular way that x-ray reflection takes place from planes with a spacing of approximately 6.2 A.U. This is probably the

TABLE 1

COLLAGEN IN WHITE, FIBROUS TISSUE (TENDON OF FOREARM, DOG)

MATERIAL	X-RAY PATTERN	D = DIST. PHOTOGRAPHIC PLATE	DIAMETER d_1, d_2, ETC., OF 1ST-, 2ND-, ETC., ORDER RINGS OR ZONES	SPACING IN A.U.	COMMENT
Fresh unstretched, moist chamber	2nd and 3rd order zones. 1st order almost coincident with centre spot	2.9 cm.	d_1 = 0.7 cm. d_2 = 1.35 d_3 = 2.0	6.0 A.U. 6.2 6.4	Liquid crystal condition with reflection from molecular planes with spacing of 6.2 A.U.
Fresh, stretched, moist chamber	Distinct arcs on 2nd order zone in stretching direction	2.9	d_1 = 1.35	3.1	Crystals in fibre formation in equilibrium with liquid crystals. Solid crystals have spacing one-half that of liquid crystals
Dried, unstretched	No zones, narrow crystal ring, usually no fibering	2.9	d_1 = 1.40	3.0	Crystals, no fibering
Dried, stretched	No zones, arcs in direction of stretching	2.9	d_1 = 1.45	2.9	Crystals with fiber formation

TABLE 2

ELASTIN (LIGAMENTUM NUCHAE DOG AND SHEEP)

MATERIAL	X-RAY PATTERN	D = DISTANCE PHOTOGRAPHIC PLATE	DIAMETER d_1, d_2, ETC., OF 1ST-, 2ND-, ETC., ORDER RINGS	SPACING IN A.U.	COMMENT
Fresh ligament, dog, unstretched	2 zones (1st order almost coincident with centre spot)	2.9 cm.	d_2 = 1.2 cm. d_3 = 1.8	7.0 A.U. 7.1	Liquid crystal condition, molecular spacing of 7.0 A.U.
Fresh ligament, dog, stretched 50–100%	Same	2.9	d_2 = 1.2 d_3 = 1.8	7.0 7.1	Same
Dried ligament, dog (stretched or unstretched)	One rather indefinite zone	2.9	d_1 = 0.9–0.95	4.6–4.0	Liquid crystal
Fresh ligament, sheep (stretched or unstretched)	Second-order zone distinct 3rd order very faint	2.9	d_2 = 1.1 d_3 = 1.7	7.6 7.5	Liquid crystal
Dried ligament, stretched or unstretched	No definite zone, possibly one with d = 0.9 cm.				

length or width of two molecules. When a living tendon is stretched some of the liquid crystals change to solid crystallites which are aligned in fibre formation, giving localized arcs or spots. As these arcs appear only on the second order zone the crystal units must be one-half the size of the double molecules of the unstretched tendon (3.1 A.U.). Therefore, when a tendon is stretched some of the collagen molecules are depolymerized forming crystallites in equilibrium with liquid crystals. If a tendon is dried the zones disappear and only crystals are left with a spacing of 2.9–3.0 A.U. These crystallites are unoriented if the tendon is dried without tension but show fibering if it is dried in a stretched condition. The change from liquid to solid crystals on drying and also the slightly smaller molecular spacing can probably be attributed to a dehydration. This spacing is approximately identical with the smallest spacing given for iso-electric gelatin. The 10.0 A.U. spacing if present would have been concealed by the central spot and there was no indication of the spacings of 4.0 and 5.5 A.U. given for gelatin by G. L. Clark and Katz, respectively.

It seems therefore that collagen exists normally in animal tissues as a liquid crystal but changes to solid crystal form on dehydration. Also, with no change in dehydration, a moist living tendon may become partially crystalline on stretching. This change from a liquid-liquid to a liquid-solid system takes place in fibrous tissue which possesses great cohesion and little power of extension and does not take place in elastic tissue. The researches of Katz[3] and G. L. Clark[1,4] have shown that crystals do not appear in rubber until it is stretched to the point where its elasticity begins to change. During the first 75 per cent of stretching rubber is a gel substance characterized by small fluidity and large elasticity, and gives equal extension for equal increments of applied force. From this point on threads, or acicular crystallites, of a strongly cohesive and much less ductile substance appear and there is a smaller elongation for a given force up to the breaking point.

It is certain that the boundary between phases is the seat of surface tension forces and probably of electrical forces as well. Too little is known about the surface tension at a solid-liquid interface to enter into much speculation on this point but calculations for calcium sulphate and barium sulphate give values in the neighborhood of 1000 to 4000 dyne/cm. and researches on the tensile strength of metals indicate a very high surface tension force between the metal crystallites and the amorphous material in which they are imbedded. It is probable therefore that when crystallization begins, there is a creation of surface energy which may be very large if the growth takes the form of small crystals. Thus a sudden change from a liquid-liquid to a liquid-solid system would mean a great increase in cohesion and a greatly increased resistance to extension. The appearance of crystals in tendons, on stretching, would therefore produce

an increase in cohesion and resistance to extension and account for the strength and rigidity of fibrous tissue, just as the presence of oriented crystals in silk and natural cellulose fibres increases their strength and durability.

Elastic tissue does not form crystals with moderate stretching although they may appear at the limit of extension. Contrary to Herzog and Gonell[6] the x-ray diagram for elastin gives a different molecular spacing from collagen. The ligamentum nuchae of the sheep gives a larger spacing than white fibrous tissue and the ligamentum nuchae of the dog, where elastic tissue is less well developed, has a molecular spacing intermediate between the other two. The zones due to elastin disappear on drying and the very indefinite zone left with the dried ligament may be due to fat or fatty acid molecules as the dried ligament, especially in the dog, is very greasy and the spacing of 4.0–4.6 A.U. is in the neighborhood of the dimensions given for the diameters of some of the fat and fatty acid molecules.

Conclusion.—X-ray pin-hole diagrams with fresh, moist tendons and ligaments show that collagen and elastin exist normally in liquid crystal form but that collagen undergoes a reversible crystallization in tendons when they are stretched. The formation of solid crystallites in a stretched tendon probably increases its cohesion and marks the limit of its elasticity.

[1] Clark, G. L., *Radiology*, **10**, 1928, 185.

[2] Clark, J. H., *Amer. Jour. Physiol.*, **82**, 1927, 181.

[3] Katz, J. R., *Kolloid Zeit.*, **36**, 1925, 300; **37**, 1925, 19. *Naturwiss.*, **13**, 1925, 410.

[4] Clark, G. L., *Applied X-Rays*, **1927**, McGraw-Hill.

[5] Katz, J. R., and O. Gerngross, *Naturwiss.*, **13**, 1925, 900. *Kolloid Zeit.*, **39**, 1926, 180. Gerngross, O., and J. R. Katz, *Kolloid Zeit.*, **39**, 1926, 181.

[6] Herzog, R. O., and Gonell, *Ber. Deutsche Chem. Gesell.*, **58**, 1925, 2228.

AN INTERPRETATION OF EXCITATION, EXHAUSTION AND DEATH IN TERMS OF PHYSICAL CONSTANTS

BY G. W. CRILE, AMY F. ROWLAND AND MARIA TELKES

CLEVELAND CLINIC, CLEVELAND, OHIO

Read before the Academy April 24, 1928

In previous publications[1] it has been shown that in excitation and exhaustion, as revealed by the microscope, marked changes occur in the different cells and tissues, notably in the brain and liver, these changes being especially manifested by alterations in size and in differential stainability. We have also found that in excitation and exhaustion the electric conductivity, capacity and temperature of different tissues, notably of the brain and of the liver, are altered.[2,3]

These and other considerations have suggested that the biologic units

or cells of which the organs of animals are constituted, are essentially microscopic electric cells. If this assumption is correct, then one would expect to find that in excitation, exhaustion and death the potential difference between the nucleus and cytoplasm of individual cells and between the different organs and tissues would be altered and that these potential differences would disappear at death.

The following investigations have been made to test this hypothesis.

That potential difference between different parts of living organisms can be measured has long been known. The P.D. between an injured and an uninjured part of the same tissue is generally indicated by the term, "action potential," or "action current." In experiments which have generally been made on surviving tissues shortly after excision from the animal, it has been found that the P.D. changes when the tissue is perfused with or immersed in different solutions. That P.D. measurements can be made on the living animal has been shown by Cannon. In such a case the P.D. which is measured is equivalent to the sum total of all the potential differences which exist in the animal between the two points where the electrodes are placed. In case the electrodes are not made of the same material, the P.D. between the two electrodes has to be considered, because if the external measuring circuit is asymmetrical from an electrical point of view, a P.D. arises at the liquid-metal junctions.

The aim of our experiments was to measure the potential difference between the different tissues of a living animal and to see how this potential difference changes when the animal is influenced physiologically. (By physiological influence we mean the intravenous injection of therapeutic and lethal doses of different agents or the application of other physical actions which cause stimulation or exhaustion.) To be able to compare P.D. changes between different organs, one electrode was placed on the subcutaneous fascia and the other electrodes were placed on the injured and uninjured parts of different tissues. By means of a switch, any pair of electrodes could be connected to the measuring device. The electrodes used were calomel electrodes with an attachment (glass tubing) filled with Ringer's solution or blood serum. P.D. measurements were made in the usual way with a potentiometer.

Experiments were made on male rabbits which had been anesthetized with urethan. The values of the potential differences obtained can be reproduced in different animals within the limits of about 25 per cent. Naturally, the general health of the animal and its general metabolic condition, the season of the year and other factors have an influence on the P.D. between the different tissues. As we shall see later, there are certain characteristic P.D. changes which can be reproduced very well. There are many possible explanations of these P.D. changes. According to Nernst's theory the P.D. of a biological system can be traced back to the

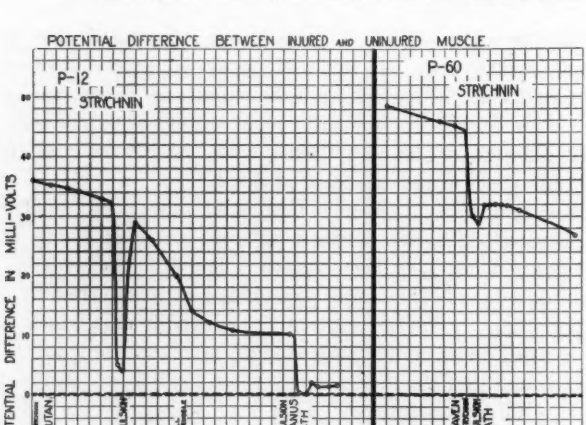

FIGURE 1

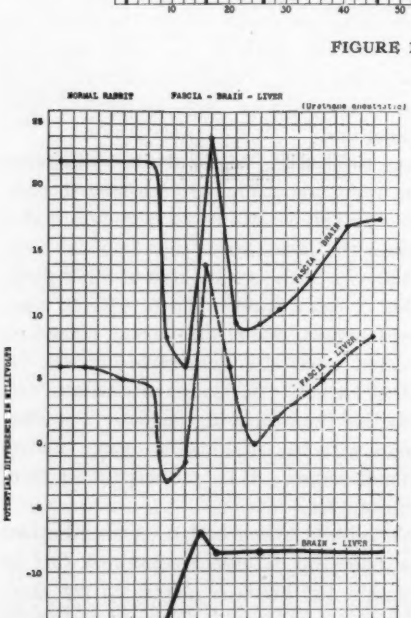

FIGURE 2

ionic concentrations. If the animal is influenced physiologically there may be a shift in the ionic concentration in the cells of the different tissues; or there may be a change in cell permeability and a change in P.D. may be caused by both phenomena.

Figure 1 shows the effect of strychnin on the P.D. between an uninjured and an injured part of the muscle (latissimus dorsi). About ten minutes after a hypodermic injection of strychnin, the animal had a violent convulsion during which the P.D. fell considerably. When the animal recovered from the convulsion, the P.D. rose to its normal value. Afterward it decreased until a final convulsion resulted in tetanus and death. At this latter point the

P.D. fell to zero. When a new incision was made in the muscle, and the P.D. was again measured, the value was found to be very small. This would indicate that during output of energy, the P.D. is lowered, showing an interesting analogy to an electric battery.

Figure 2 shows the effect of adrenalin on the P.D. of the brain and liver. The great stimulating effect of adrenalin causes a fall in P.D., followed by a rise, a subsequent decrease and a final increase to almost the original value. The amount of the P.D. between the normal fascia and the brain is not the same as that

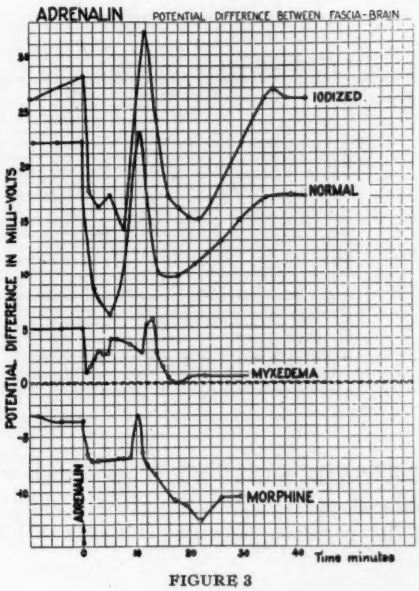

FIGURE 3

in an iodized, a myxedematous or a morphinized animal, and the changes in P.D. due to adrenalin vary (Fig. 3).

In higher animals sleep is essential to life. Rabbits usually die after from 90 to 120 hours of insomnia. During insomnia the animal steadily loses energy until death occurs quietly. The potential differences between the brain and the fascia of animals kept awake until near the final stage are shown in figure 4. In this figure the P.D. changes produced by adrenalin in animals kept awake are compared with the changes in normal animals. Not only are the changes due to adrenalin much smaller in the former group of animals,

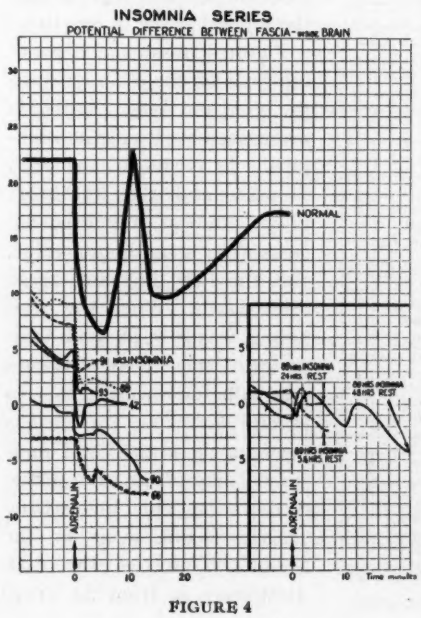

FIGURE 4

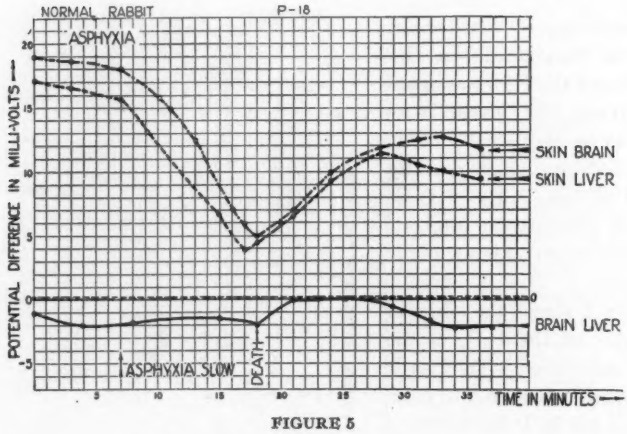

FIGURE 5

but also the amount of P.D. as a whole is much smaller. Even when an animal was permitted to rest for a while the P.D. remained close to zero. (The negative potential indicates that the fascia became negative and the injured part of the brain became positive. In most cases the fascia is positive and the injured tissue is negative.)

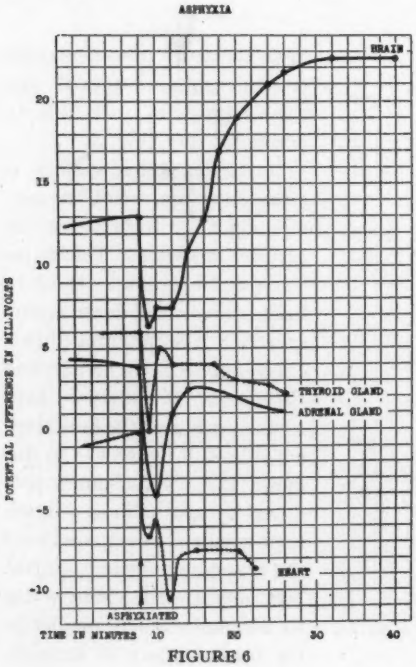

FIGURE 6

Figure 5 shows the effect of asphyxia on the P.D. between the brain and liver. Asphyxia was caused by closing the windpipe. As is shown, the P.D. decreases and when the heart ceases to beat, the P.D. decreases to a minimum value. But the P.D. increases again after death. When the dead animal was kept at room temperature, the P.D. of all tissues gradually fell toward zero. In several hours no P.D. exists between the injured and uninjured parts of the same tissue except in the voluntary muscles. But even in the voluntary muscles the P.D. disappears in from 20 to 40

hours. The disappearance of the P.D. indicates the complete or definitive death of the tissue in contrast with clinical death.

In figure 6 we see the changes in P.D. in different organs when the animal

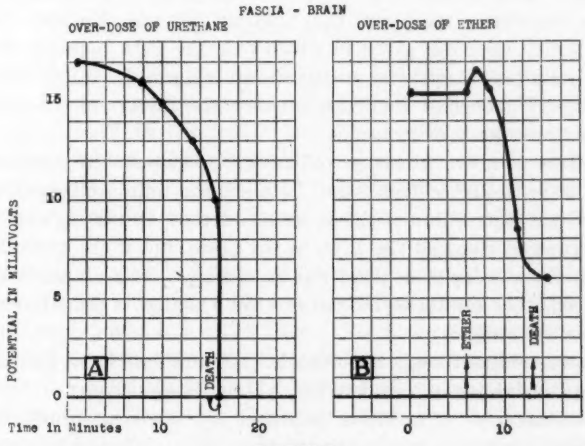

FIGURE 7

is killed by asphyxia. We know that during asphyxia there is an increased secretion of adrenalin. Whether the decrease in P.D. is caused by the se-

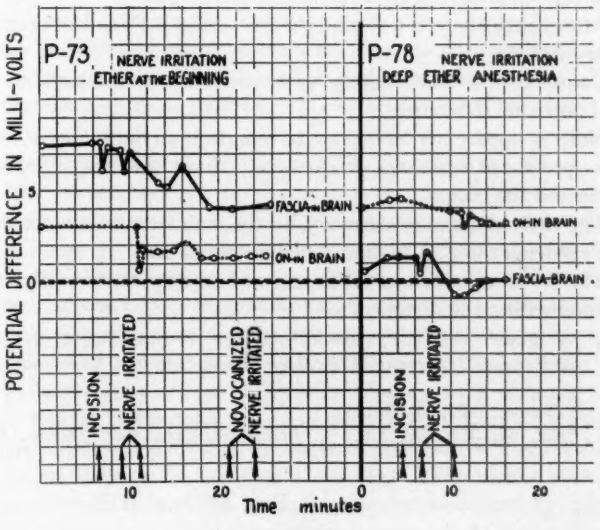

FIGURE 8

cretion of adrenalin or whether death is associated with a temporary fall in P.D., we cannot as yet say. But there is no doubt, when the animal is killed by asphyxia, that at the moment of death its potential falls to a minimum value—near zero. Each tissue as it dies loses its potential.

As for anesthesia, we found that urethan did not diminish the P.D. unless a lethal dose was given in which case the P.D. between the fascia and the brain fell abruptly to zero as shown in figure 7. Light ether anesthesia slightly increased the P.D. between the fascia and the brain but deep ether anesthesia decreased it.

The effect of nerve irritation on the P.D. between the fascia and the injured brain (injury current) and between the uninjured surface of the brain and the injured brain (demarcation current) can be seen in figure 8. Nerve irritation changed the P.D. in the brain, but if the nerve had previously been novocainized, there was no change. As is shown in the same figure, deep ether anesthesia did not prevent a change in potential when the nerve was irritated.

Summary.—Experiments on animals (100 rabbits) have indicated the following conclusions in regard to the P.D. in living tissues:

1. Excitation or stimulation produced by physical injury, drugs or other agents causes an immediate fall in the P.D., followed by a rise. Repeated or protracted excitation tends to diminish the P.D.; and when the P.D. approaches zero, death occurs.

2. Anesthetics, narcotics, hemorrhage, asphyxia diminish the P.D. progressively until as it approaches zero death occurs.

3. After death there is a secondary rise of the P.D. in the brain and in voluntary muscle.

4. Consciousness and activity apparently are maintained at the expense of potential differences.

5. Sleep is apparently necessary to maintain a continuous P.D. in the brain, as prolonged insomnia progressively diminishes the P.D. between the fascia and the brain.

6. The thyroid gland is necessary for the maintenance of a normal P.D., for in myxedema the P.D. is diminished nearly to zero.

7. The life of an organism exists only as long as potential differences are maintained within the organism.

[1] *Proc. Soc. Exper. Biol. Med.*, 1909–10, **7**, 87–88. *Tr. Am. Surg. Assoc.*, 1910, **28**, 553–559. *A Physical Interpretation of Shock, Exhaustion and Restoration*, London, **1921.**

[2] *Am. J. Physiol.*, 1922, **60**, 59–106.

[3] *Ibid.*, 1922, **62**, 341, 349, 370. *J. Pharmacol. and Exper. Therap.*, 1923, **21**, 429–442.

THE POLARIZATION OF CHARACTERISTIC RADIATION

BY J. A. BEARDEN

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The polarization of the general radiation from an x-ray tube has been studied by several experimenters.[1] In general it has been found that the shorter wave-lengths of the general radiation are more strongly polarized than the longer wave-lengths. As the cathode ray velocity is increased the polarization is however decreased. Experiments by Barkla[1] and others on fluorescent radiation have indicated that the characteristic radiation is unpolarized.

Bishop,[2] using a unique scheme of filtering the radiation from a molybdenum target x-ray tube, has made a series of measurements of the polarization of the molybdenum $K\alpha$ radiation. In all his measurements he has found a partial polarization of this radiation. If this is a true effect it constitutes the most fundamental difference between the characteristic radiation from an element used as anticathode and the fluorescent rays from the same element. Since a large part of the characteristic radiation from a tube is fluorescent it would indicate that the characteristic radiation directly excited must be very strongly polarized.

The importance of knowing the exact magnitude of the polarization of the characteristic x-rays seems to warrant a repetition of Bishop's[2] experiment with filtered x-rays, but under more favorable conditions. It has also been found possible to make accurate polarization measurements using a monochromatic ($K\alpha$ line reflected from a calcite crystal) beam of x-rays, thereby eliminating the uncertainty of the effect due to the general radiation.

The apparatus used in the first part of this experiment is shown in figure 1. X-rays from a water-cooled molybdenum tube, placed directly above the Bragg spectrometer and in a nearly horizontal position, were collimated by slits S_1 and S_2 about 0.5 mm. in diameter. Between the slits was placed a double filter system F_1F_2 on a slide F. The filter F_1 was made of strontium oxide and F_2 of zirconium oxide. The filters were matched by Barrett very precisely according to the method suggested by Ross. The intensity of the $K\alpha$ line is about 85 to 90% of the total intensity transmitted by the system. The beam fell vertically on a graphite block G $1/8''$ thick and $2''$ in diameter placed at the center of the Bragg Spectrometer. The block was placed at an angle of 45° to the x-ray beam, and facing the window of the ionization chamber. The chamber was filled with methyl bromide, and the ionization current measured by a sensitive Compton electrometer. A is a screen for protecting the ionization cham-

ber from stray radiation. The tube was operated at about 50 kv. and 1 to 40 *ma*.

In taking the readings the ionization chamber was first placed in position I_1 (parallel to the cathode rays). The intensity of the rays scattered by the graphite block was measured for each filter F_1 and F_2. The chamber and scatterer were then moved to position $I_\perp$ (perpendicular to the cathode rays, not shown in the figures) and similar measurements taken. Likewise for position I_3 (parallel to cathode rays). The difference of the intensity $F_2 - F_1$ for each setting of the ionization chamber gave the scattering due to the $K\alpha$ radiation of molybdenum plus about 10 or 15% general radia-

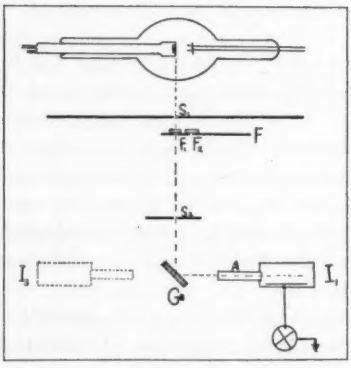

FIGURE 1

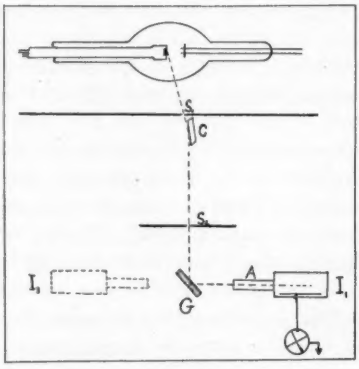

FIGURE 2

Diagram of apparatus.

tion. The intensity in positions I_1 and I_3 were accurately the same. Putting $\frac{I_1 + I_3}{2} = I_{||}$ it was found that the ratio $\frac{I_\perp}{I_{||}}$ for 33 sets of readings was

$$\frac{I_\perp}{I_{||}} = 1.028 \pm 0.005.$$

In order to test the geometric symmetry of the apparatus the following method was used. A fluorescent radiator of strontium oxide was put in place of the graphite scattering block G. The excitation of fluorescent radiation not being influenced by the polarization of the primary rays one would get the same intensity for the three positions of the ionization chamber as used above. Measurements taken with and without the filters gave very precisely

$$\frac{I_\perp}{I_{||}} = 1.000,$$

showing that there was no lack of symmetry in the apparatus. The results thus indicate a polarization of the rays which is greater than the experimental error. At least a part of the polarization can however be ascribed to the general radiation which was present with the molybdenum $K\alpha$ radiation.

A further test was made by arranging the apparatus as shown in figure 2. A calcite crystal was put in place of the filters F_1F_2 and the target of the x-ray tube adjusted so that the crystal reflected the molybdenum $K\alpha$ line vertically down to the center of the spectrometer. Slit S_1 was 2 mm. wide and S_2 was 0.5 mm. by 10 mm. The radiation fell on the graphite block G as before. The block was rotated with the ionization chamber so that the same amount of the graphite was scattering in each position and the distance traversed by the rays was the same in the three positions. The opening in the ionization chamber was about 20 mm. in diameter and about 15.75 cm. from the center of the scattering block. The average of 48 sets of measurements gave

$$\frac{I_\perp}{I_\parallel} = 0.984 \pm 0.003.$$

Another series of measurements using a strontium oxide fluorescent radiator as above gave

$$\frac{I_\perp}{I_\parallel} = 1.021 \pm 0.002.$$

Combining this correction with the measured ratio one gets the true ratio

$$\frac{I_\perp}{I_\parallel} = 0.965.$$

The intensity in this case is greater in the direction of the cathode rays. If the x-rays were unpolarized the ratio should be $\frac{I_\perp}{I_\parallel} = 0.972$ due to polarization introduced by the crystal. Correcting the observed ratio for the polarization introduced by the crystal one gets

$$\frac{I_\perp}{I_\parallel} = 0.993 \pm 0.004.$$

The difference between this value and 1, which it should be for unpolarized x-rays, is within the experimental error.

In the case of the filtered radiation there appears to be a slight polarization of the characteristic radiation but much smaller than the value found by Bishop.[2] In the more direct method using a crystal for separating out the K_α radiation there is no indication of any polarization of the characteristic radiation.

Kirkpatrick's[3] method of using crystal reflection to measure the polarization is not as satisfactory as the present method because the intensity reflected by a crystal depends so greatly on the geometric symmetry of the apparatus. By using two reflecting crystals, as is used in absolute intensity measurements, a more accurate determination might be made than with a single crystal. It seems however that the results obtained by the more direct method used by the writer should be more reliable than those obtained by either of these methods.

My results thus indicate that the characteristic radiation from an x-ray tube is probably unpolarized. This result is in good accord with the ordinary ideas of x-ray production, and also with the recent results on the polarization of fluorescent radiation by Compton.[4] The criticism of Kirkpatrick[3] that the polarization factor in the formula for the intensity of x-ray reflection has not been used correctly by many writers accordingly applies only to discussions in which the general radiation from an x-ray tube was used.

[1] O. G. Barkla, *Roy. Soc. Proc.*, **77A**, 247 (1906). H. Haga, *Ann. der Physik*, **28**, 439 (1906). P. A. Ross, *Am. Phys. Soc. Bull.*, **1**, No. 10. Kirkpatrick, *Phys. Rev.*, **28**, 625 (1926).

[2] J. B. Bishop, *Phys. Rev.*, **28**, 625 (1926).

[3] Kirkpatrick, *Ibid.*, **29**, 632 (1927).

[4] A. H. Compton, elsewhere in these PROCEEDINGS.

THE REPULSION BETWEEN ELECTRIC CURRENTS AND THEIR INDUCED EDDY CURRENTS IN PARALLEL

BY CARL BARUS

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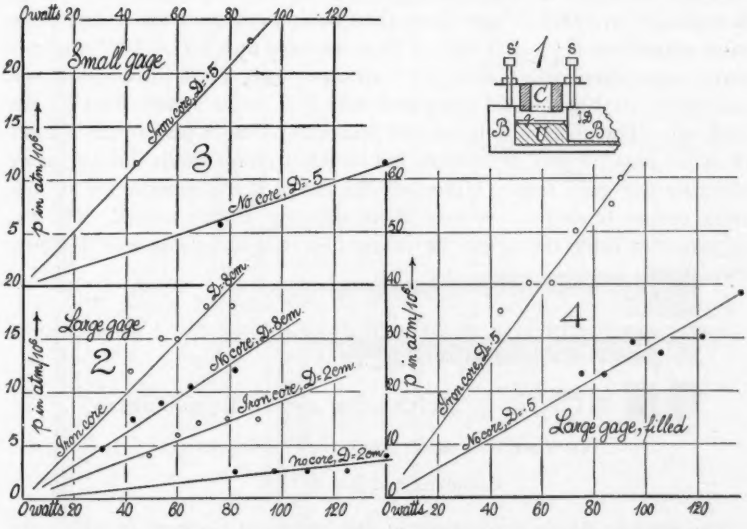
Communicated June 1, 1928

1. *Apparatus.*—The interferometer U-gage, with its two flat cylindrical pools of mercury seemed to lend itself well for measurements in relation to Elihu Thomson's phenomena and I, therefore, tested an apparatus (Fig. 1) for this purpose. Here U is the mercury in one shank of the gage, about 10 cm. diam. and 1 cm. deep, with a thin cover glass g in the block of iron B. C is an annular coil, 8 cm. external, 4 cm. in internal diameter, and 3.5 cm. high, containing about 350 turns of wire. Adjustable on 3 tripod screws, s, s', the base could be put at a distance D from the surface of U at pleasure. The coil was supplied with an alternating current of 60 cycles from the electric lighting circuit, transformed down to 10 to 30 volts. When the current circulates in C, there is a pressure on U, due to the eddy currents induced in the mercury. The coil was additionally provided with

an annular core of iron, by which the impedance could be increased from 0.5 to 1 ohm and the eddy currents correspondingly increased.

2. *Data.*—Unfortunately the results obtained with this promising arrangement were disappointing. Not only did the pressures (even for small D) rarely exceed 50×10^{-6} atm., but the mercury heads were apparently kept in oscillation, so that the fringes were soon blurred or wiped out. Both these difficulties could have been overcome by using currents of higher frequency but the requisite apparatus was not at hand.

An example of the results is given in figure 2, when the pressures observed in millionths of an atmosphere are plotted against the effective



watts fed into the coil. The data are straggling because of the difficulty in seeing the fringes just mentioned, and straight lines were therefore drawn through them. In the two upper curves the distance of the bottom of the coils was but $D = 8$ millimeters and they give the data for coils empty, and iron-cored, respectively, as indicated. In the lower curves the distance was increased to about 2 cm.

Since the diameter of the mercury troughs was about 10 cm. and the area 78 cm., the maximum repulsive force acting on the top face of the mercury would be somewhat above 1.5 grams weight.

3. *Modified Gages.*—As there was no improvement of fringes when the coil was suspended from a separate standard free from the interferometer, I finally tested the smaller gage, with cisterns 5 cm. in diameter filled with mercury to the brim (depth 2.0 cm.) to insure minimum resistance

in the mercury cylinder. The results are given in figure 3; but such a gage is much more mobile as a rule than the large gage and the points obtained from washed fringes are merely estimates. The maximum pressures observed, however, do not differ much from the preceding. Thus the average repulsive forces must have decreased as the areas of the cisterns. With these half filled almost no fringe displacement was obtained. This induced me to fill the cistern of the large gage (Fig. 1) to the brim, so that the mercury column was now 10 cm. in diameter and 2 cm. deep. Possibly from the increased inertia or from greater axial symmetry in the repulsive forces, the fringes were now clearer than before and could be followed with less difficulty even at the highest displacements. These, as indicated in figure 4, were more than twice as large as above under the same conditions ($D = 0.5$ cm.). Thus we have now 9.7×10^{-6} atm. per watt, contrasting with 0.25×10^{-6} atm. per watt for the iron-cored coil; and 0.3×10^{-6} atm./watt compared with 0.17×10^{-6} atm./watt for the free coil. The observations are still straggling, due in part to the wabble of such a massive pool of mercury but largely to some thermal discrepancy affecting the gage zero. Moreover, the fringe displacements for no obvious reason tended to oscillate about different means values. The expectation of using the device for rating dielectric constants was therefore abandoned.

APPARENT EVIDENCE OF POLARIZATION IN A BEAM OF β-RAYS

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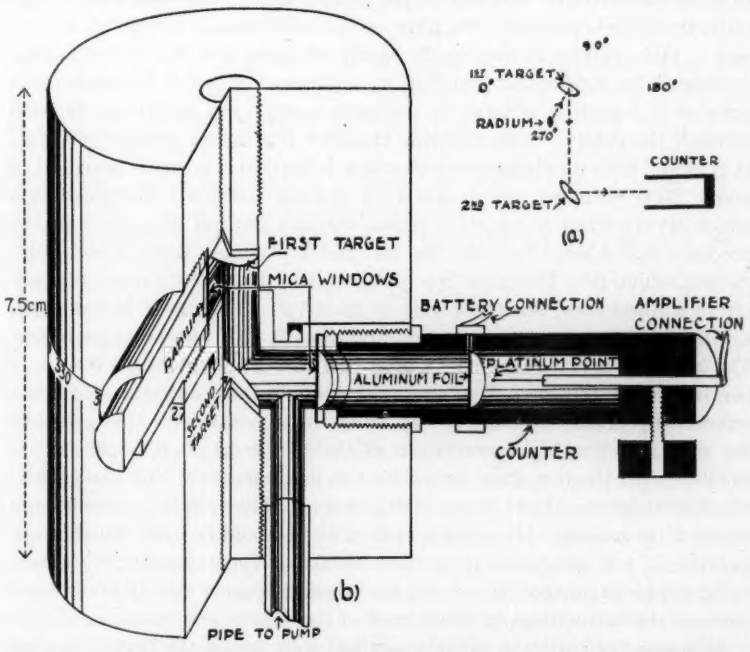
Communicated June 6, 1928

The already classic experiment of Davisson and Germer[1] in which the diffraction of electrons by a crystal shows the immediate experimental reality of the phase-waves of de Broglie and Schrödinger suggested that it might be of interest to carry out with a beam of electrons experiments analogous to optical experiments in polarization. It was anticipated that the electron spin, postulated by A. H. Compton[2] to explain the systematic curvature of the fog-tracks of β-rays, and recently so happily introduced in the theory of spectra by Uhlenbeck and Goudsmit[3] might appear in such an experiment as the analogue of a transverse vector in the optical experiments. This idea has lately been theoretically developed by C. G. Darwin.[4] Experiments in this line were undertaken over a year ago. Since they are soon to be interrupted, it seems advisable to make a preliminary report of the results obtained thus far, although they are somewhat inconclusive in spite of a great accumulation of data.

Since the equivalent wave-length in the wave mechanics of even slowly moving electrons is of the order of that of x-rays, it seemed preferable to attempt an experiment analogous to optical polarization by scattering or absorption rather than by reflection or double refraction. We have been chiefly occupied by an experiment analogous to that in which Barkla demonstrated the polarization of x-rays by double scattering. In our experiment β-particles, twice scattered at right angles, enter a Geiger counter. The relative numbers entering are noted, as the angle between



the initial and final segments of the path is varied. For reasons to be mentioned later the angles at which most of the observations have been made are those indicated in figure 1(a) as 270° and 90°. The difference between the configurations of the three segments of path at these two angles is the same as the difference between right- and left-handed rectangular axes. The apparatus in its latest form is shown in detail in figure 1(b), a quarter-section being supposed removed. Its largest part is a steel cylinder with a cylindrical passage along the axis and two others at right angles to it. The axial passage is closed at either end with a screw plug. Each plug ends in a gold scattering target set opposite one of the radial passages and at 45° to the axes of the two passages at the junction of which it is placed.

A milligram of radium, which is the source of the β-particles, is set in one of the radial passages and the counter in the other. The three passages thus form the three segments of the path of the β-particles. To obtain the required variation in angle between the initial and final segments, the cylinder is made in two parts, so that the upper part, carrying the radium and the first target, can be rotated with respect to the lower about their common axis. The parts fit together at a ground joint with a mercury seal; the two radial passages are closed with mica windows, thin enough to allow the entrance and exit of the β-particles but thick enough to sustain atmospheric pressure; the plugs in the axial passage are sealed in with wax. The cylinder is thus made nearly air-tight and the cavity is kept evacuated by continuous pumping to a pressure at which the mean free path of a β-particle is large in comparison with the length of its path through the cavity. The counting chamber is a hollow ebonite cylinder. It is closed with an aluminum foil, which is kept at a positive potential of about 2000 volts by connection to a storage battery. The ionization which occurs when a β-particle passes through the foil into the chamber produces a discharge between the foil and a platinum point a few millimeters behind it. The point is a platinum wire two mils in diameter ending in a fused knob about six mils in diameter. This point is connected through a high resistance to ground and directly to a four-stage amplifier. The amplifier operates a sensitive relay, which in turn actuates a recording pen on a moving tape. Discharges are produced not only by β-particles but also by photo-electrons ejected from the apparatus by the γ-rays of the radium. The high penetration of these rays makes it impossible to shield against them without interposing so much material that the path of the β-particles would be too much lengthened. Their effect is considerably reduced by making the counting chamber of ebonite, from which comparatively few photo-electrons are ejected. Their number, however, could not be neglected, but there is no reason to expect that it would vary between the two settings at which most of the counts were made.

Although the platinum points described were found the best of several types and materials that were tried, they are far from satisfactory. They usually give inconsistent results after an hour or two of use and have to be replaced. Moreover, the counts obtained with two different points do not agree. For this reason and on account of the uncertainty of the effect of the γ-rays, it seemed inadvisable to attempt counts all around the circle. Attention was given instead to taking counts to test an early observation that fewer β-particles were recorded with the radium at 90° than at 270°. Data are taken as follows. A count is taken at one setting for a definite time (five or ten minutes) and then at the other setting for an equal time. This is continued usually as long as the counter gives self-consistent results. To offset the effect of small gradual changes in the characteristics

of the counter and in the voltage of the battery, the count at one setting is compared with the counts immediately preceding and following it at the other setting. Thus, for example, from eleven counts five values are obtained for the ratio of the count at one setting to the count at the other. The mean of these values is taken and the probable error computed in the usual way. It is these means and probable errors that are given in the following table. It must be admitted that the probable error in many cases is reckoned from too few values to give it great validity. The table shows the results of nineteen sets of data.

Count at 90° / Count at 270°	..	..	..	..	0.76	0.90	0.94	0.87	0.98	1.03
Count at 90° / Count at 0°	0.78	0.62	0.65	..	..	..	..	..	..	..
Count at 0° / Count at 270°	..	..	..	0.87	..	..	..	..	..	..
Probable error	0.01	0.02	0.01	0.02	0.01	0.07	0.01	0.02	0.01	0.03
Count at 90° / Count at 270°		1.03	0.91	0.95	0.99	1.01	1.06	1.05	0.55	0.91
Probable error		0.02	0.02	0.05	0.03	0.04	0.05	0.02	0.05	0.03

It will be noted that of these results a large part indicate a marked asymmetry in the sense already mentioned. The rest show no asymmetry beyond the order of the probable error. The wide divergence among the results calls for some explanation, and a suggestion to this end will be offered later. Meanwhile a few remarks may be made on the qualitative evidence of asymmetry. Since the apparatus is symmetrical in design as between the two settings at 90° and 270°, the source of the asymmetry must be looked for in an accidental asymmetry in construction or in some asymmetry in the electron itself. The following possibilities may be suggested in the former case. The radium and the point in the counter were doubtless not exactly centered. But they were removed and replaced repeatedly in the course of the observations, and it seems unlikely that their accidental dislocations could be so preponderantly in one direction as are the observations. Any effect due to this cause could be offset by turning the counter and the rod that carries the radium through 180°. The apparatus with which these data were obtained was not designed to make this convenient, but in the latest apparatus these rotations can be made without disturbing anything else. The results thus far obtained with this apparatus do not lead us to believe that this factor is effective. There was doubtless some asymmetry in the targets as regards their orientation and surface condition. These also were several times removed and replaced

after their surfaces had been freshly filed bright. A magnetic field inside the cavity due either to the slight penetration of the earth's field through the steel walls or to an accidental magnetization of the cylinder itself would introduce an asymmetrical factor. It seems highly unlikely, however, that any deflection so caused could be great enough to produce effects of the magnitude observed. It seems possible, on the other hand, that a spinning electron might be oriented by even a weak field by a kind of space quantization and that this orientation might combine with the scattering to produce the observed asymmetry. This explanation, of course, assumes a polarity in the electron as definite as that required to explain the observations as due to double scattering. Of the same sort is the supposition that the beam of β-particles undergoes a polarization in passing through the mica windows, similar to the polarization of light in passing through a tourmaline crystal. This effect was in fact looked for carefully in an experiment auxiliary to the present investigation but it was not found.

It should be remarked of several of these suggested explanations of the observations that their acceptance would offer greater difficulties in accounting for the discrepancies among the different results than would the acceptance of the hypothesis that we have here a true polarization due to the double scattering of asymmetrical electrons. This latter hypothesis seems the most tenable at the present time. The discrepancies observed we ascribe tentatively to a selective action in the platinum points, whereby some points register only the slower β-particles. Observations in apparent agreement with this assumption have recently been made by N. Riehl.[5] It is necessary to suppose further that the polarization is also selective, the effect being manifest only in the faster β-particles. In support of this it may be remarked that a few observations we have just made seem to show that asymmetry is more consistently observed when a piece of celluloid or cellophane is placed in front of the counter to stop the slower β-particles. Perhaps the simplest assumption here is that only β-particles which are scattered without loss of energy show polarization.

We have made no attempt at a theoretical treatment of double scattering beyond a consideration of the question whether the results here reported are of an asymmetry of higher order than what might be expected of a spinning electron. The following suggestion is then offered not at all as a theory of the phenomenon but merely as a remark on the geometry of the experiment. If it be supposed that the spin vector of a moving electron is always at right angles to its velocity vector, and that when the electron is scattered at right angles its new velocity vector has the direction of the vector product of its former velocity and spin vectors and its new spin vector has the direction of its former velocity vector, then the observations here described will be qualitatively accounted for.

In closing we wish to acknowledge gratefully our indebtedness, for help and advice in the construction of Geiger counters, to Dr. C. W. Hewlett of the General Electric Company, to Mr. A. E. Loomis of the Loomis Laboratory and to Dr. L. F. Curtiss of the Bureau of Standards. We are under obligation also to Mr. Hermann Beck for his interest and care in the construction of the apparatus used.

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THE SPECTRUM AND STATE OF POLARIZATION OF FLUORESCENT X-RAYS

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A brilliant series of experiments by Barkla and Sadler,[1] begun in 1907, showed the now well-known phenomenon of fluorescent x-rays, excited in the heavier elements when traversed by primary x-rays of shorter wavelength. They identified two series of such fluorescent rays, which they called K and L radiations. With the advent of crystal spectrometry, the Braggs[2] and Moseley and Darwin[3] showed that the absorption coefficients of the lines in the x-ray spectra were the same as the absorption coefficients which Barkla and Sadler had found for their fluorescent radiations, thus identifying the fluorescent K and L series radiations with the characteristic line radiation which comes directly from the target of an x-ray tube. This identification was made more definite when spectra of the fluorescent rays were obtained, which showed the same lines as those present in the direct rays. Such spectra have been published, for example, by Duane and Shimizu,[4] Clark and Duane,[5] Woo[6] and D. L. Webster.[7]

In Sadler's earliest studies of the fluorescent rays,[8] he finds by absorption measurements that under favorable conditions not more than 1 per cent of the secondary rays from a fluorescing radiator are scattered. The spectra of Clark and Duane,[5] however, indicate that with fluorescent radiators of barium, lanthanum, molybdenum and silver, excited by x-rays produced at about 90 kv., less than 4 per cent of the secondary radiation consists of the homogeneous fluorescent rays. Woo's spectra, on the other hand, show

only a strong line spectrum with no indication of any continuous spectrum mixed with the fluorescent rays.

In figure 2 is shown a spectrum of the fluorescent x-rays from silver, excited by x-rays from a tube with a tungsten target, operated at 53 kv. The apparatus was arranged as shown in figure 1, which is drawn approximately to scale. In order to detect, if possible, any continuous spectrum, the slits collimating the beam incident on the crystal were made rather wide, as is indicated by the width of the α and β lines. Perhaps the most striking feature in the spectrum is the complete absence of any continuous spectrum. In fact an estimate of the ratio of the energy in the continuous

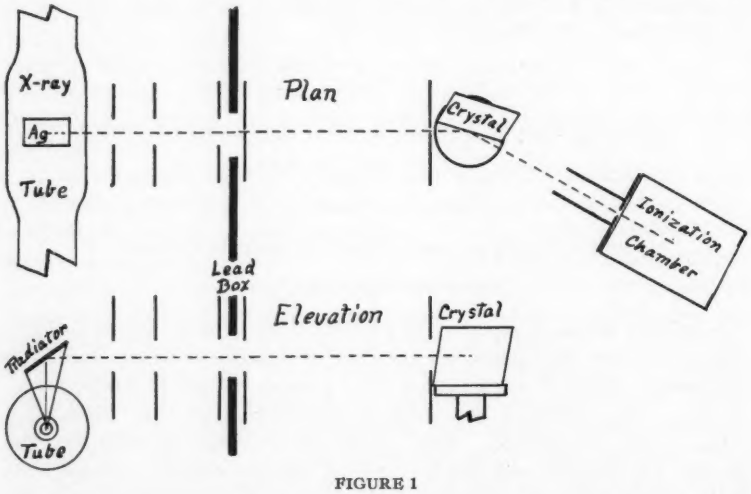

FIGURE 1

spectrum to that in the line spectrum from these data gives 0.007 ± 0.01. New absorption measurements indicate also that the line radiation constitutes more than 99 per cent of the total radiation. These results are in complete agreement with the early findings of Sadler, and suggest that the greater part of the radiation studied by Clark and Duane was not really the secondary rays from the radiator under investigation.

It is worthwhile calling attention again, as Barkla has done long ago, to the value of these fluorescent rays as a source of homogeneous x-rays. If the presence of the β and γ lines is objectionable, they can be removed by a suitable filter, leaving practically nothing except the $K\alpha$ radiation. The homogeneity thus secured is more complete than that usually got by crystal reflection. When homogeneity is sought by filtering the direct beam from a molybdenum target through a zirconium filter, under the best conditions only about 25 per cent of the transmitted radiation is of

the $K\alpha$ type.[9] By filtering the fluorescent beam, on the other hand, the homogeneity may be made as great as 98 per cent.

Under the conditions of the present experiment, the intensity of the fluorescent rays as measured at the ionization chamber was approximately $^1/_{200}$ of that of the primary beam. The rays were easily visible with the fluorscope.

Ratio of the α to the β Lines.—The ratio of the area of the α peak to that of the β peak from these experiments is 4.58. When this is corrected for:

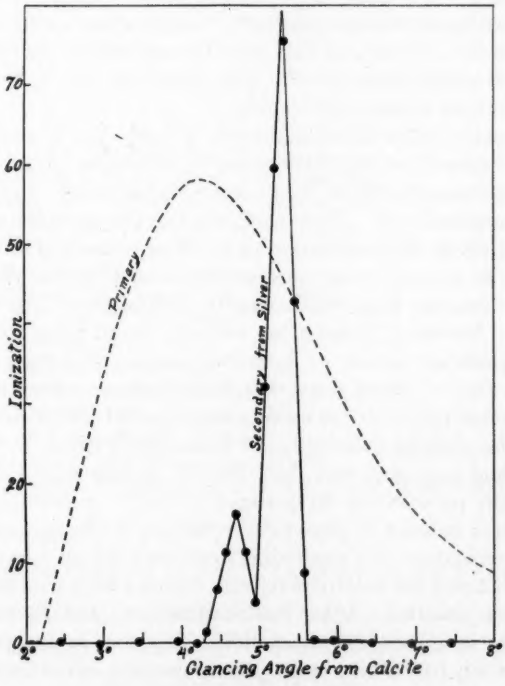

FIGURE 2

(1) the difference in ionization per unit intensity for the two wave-lengths (the method of calculating this correction will be discussed in a later paper), a factor of 0.825; (2) the difference in the absorption of the α and β lines in the air and in the fluorescent radiator, factor 1.10; and (3) the difference in the reflecting power of the crystal for the two types of radiation, a factor of 1.08, the ratio of the energies of the two lines as emitted from the silver atoms in the radiator becomes 4.5. This agrees within the errors of experiment and correction with Unnewehr's ratio[10]

of 4.65 for the α and β lines from a silver target. Thus the relative intensity as well as the positions of the spectrum lines is approximately the same in the fluorescent as in the primary x-rays.

Unpolarized Character of Fluorescent X-Rays.—In their earliest experiments on the characteristic secondary radiation, Barkla and Sadler tested for a possible polarization of the rays by using a radiator which emitted strong fluorescent radiation as an "analyzer" for the direct rays from an x-ray tube.[11] A carbon scattering block used as analyzer reveals in this case some 15 per cent polarization of the primary beam. They were unable, however, to detect any polarization when a fluorescing radiator was used as analyzer. If the probable error of their measurements was 1 or 2 per cent, this would mean that the polarization of the fluorescent rays is probably less than about 10 per cent.

More recently, Mark and Szilard,[12] in a study of the x-rays polarized by reflection from a crystal, have found no indication of analysis of these rays by a fluorescing radiator except insofar as scattered rays were mixed with the fluorescent rays. Their method was a photographic one.

The question of the polarization of the fluorescent x-rays has acquired new interest as a result of Bishop's conclusion that the line radiation from the target of an x-ray tube, which is partly of fluorescent origin, is partially polarized.[13] Moreover, Raman has recently found a type of secondary light rays which are similar to fluorescent rays in that their wave-length differs from that of the primary rays, but which are strongly polarized.[14] It thus becomes important to make a more careful test than has hitherto been made for possible polarization of fluorescent x-rays.

The method employed was that used by Hagenow and the writer in examining the polarization of scattered x-rays.[15] A horizontal beam of x-rays struck a radiator R_1 placed above the axis of a Bragg x-ray spectrometer. The secondary rays proceeding downward fell on a second radiator R_2, also placed over the spectrometer axis, but on a level with the window of the ionization chamber. When both radiators R_1 and R_2 were plates of graphite, the ionization current with the chamber in the perpendicular position was only 0.09 of that in the parallel position, indicating almost complete polarization. When R_1 was silver and R_2 graphite,

$$\frac{i_\perp}{i_\parallel} = 0.968. \qquad (a)$$

When R_1 was silver and R_2 a plate of compressed ZrO, the observed ratio was

$$\frac{i_\perp}{i_\parallel} = 0.964. \qquad (b)$$

An auxiliary experiment showed that the zirconium oxide analyzer gave almost the same intensity in the $\parallel$ and $\perp$ positions even when struck

by rays polarized by scattering from carbon. The ratio 0.964 observed in case b is thus to be ascribed to the lack of geometric symmetry in the $\parallel$ and $\perp$ positions. The corrected value of the intensities in the two positions is thus

$$\frac{\perp}{\parallel} = \frac{a}{b} = \frac{0.968}{0.964} = 1.004$$

with a probable error, estimated from the variations of the readings, of ± 0.005.

This means that the characteristic fluorescent x-rays from silver are completely unpolarized, within a probable error of 0.5 per cent. It follows that any polarization in the line spectrum of the primary x-rays must be due to the portion of the rays resulting from the direct action of the cathode rays.

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AN INTERPRETATION OF DIRAC'S THEORY OF THE ELECTRON

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Dirac's[1] theory of the electron starts out with the following premises: (*a*) The wave-equation must be linear in form, (*b*) the equation must satisfy the requirements of special relativity and (*c*) for a free electron the results must be identical with those given by the Schroedinger-Gordon wave-equation. He finds it possible to satisfy all of these conditions by introducing into the wave-equation matrix-operators which are very similar to those used by Pauli[2] in the formulation of the theory of the spinning electron. As is well known, this theory of Dirac's is promising to be very significant because it eliminates the necessity of introducing assumptions

about the electron's spin and gives from its simple and general premises all the required empirical results.

Comparing Dirac's considerations with those of Pauli (loc. cit.), it becomes obvious that Dirac's matrix-operators have not yet been labelled with physical names to their full extent. It is the purpose of this note to associate definite physical quantities with Dirac's α_1, α_2, α_3 and to make the analogy with Pauli's treatment more complete. The result is that α_1, α_2, α_3 may be thought of as operational matrix-representations of the velocity-vector $\dot{x}/c$, $\dot{y}/c$, $\dot{z}/c$ in the same sense as Pauli's s_x, s_y, s_z represent the spin.

For an electron having a charge $(-e)$ the classical Hamiltonian function H is related to the momenta p_x, p_y, p_z by the equation

$$\frac{H}{c} + \frac{eA_0}{c} = \sqrt{m^2c^2 + \left(p_x + \frac{eA_x}{c}\right)^2 + \left(p_y + \frac{eA_y}{c}\right)^2 + \left(p_z + \frac{eA_z}{c}\right)^2}$$

where A_0, (A_x, A_y, A_z) are, respectively, the electrostatic and the vector-potentials of the field. It is well known that another way of writing this is

$$\frac{H}{c} + \frac{eA_0}{c} = mc\sqrt{1-\beta^2} + \frac{\dot{x}}{c}\left(p_x + \frac{eA_x}{c}\right) + \frac{\dot{y}}{c}\left(p_y + \frac{eA_y}{c}\right) + \frac{\dot{z}}{c}\left(p_z + \frac{eA_z}{c}\right). \quad (1)$$

This, in fact, is the form at which one usually arrives first in the derivation of the Hamiltonian function as $H = \Sigma\, p\dot{q} - L$, where L is the Lagrangian function. Comparing this with Dirac's equation

$$\left\{p_0 + \frac{eA_0}{c} + \alpha^{(1)}\left(p_x + \frac{eA_x}{c}\right) + \alpha^{(2)}\left(p_y + \frac{eA_y}{c}\right) + \alpha^{(3)}\left(p_z + \frac{eA_z}{c}\right) + \alpha^{(4)}\, mc\right\}\psi = 0 \quad (2)$$

we see that letting

$$p_0 = \frac{H}{c},\ \alpha^{(1)} = -\frac{\dot{x}}{c},\ \alpha^{(2)} = -\frac{\dot{y}}{c},\ \alpha^{(3)} = -\frac{\dot{z}}{c},\ \alpha^{(4)} = -\sqrt{1-\beta^2}.$$

We can derive (2) from (1) according to the rules which Pauli used in deriving the equations of the spinning electron. In fact, Pauli's rule is the following. Let the classical Hamiltonian equation be

$$H\,(p_k, q_k, s^{(1)}, s^{(2)}, s^{(3)}, \ldots) = E \quad (3)$$

where $s^{(1)}$, $s^{(2)}$, $s^{(3)}$, . . . represent variables which are required to have definite characteristic values. The Schroedinger equation is obtained from this by writing

$$H\left(\frac{h}{2\pi i}\frac{\partial}{\partial q_k}, q_k, \mathbf{s}^{(1)}, \mathbf{s}^{(2)}, \mathbf{s}^{(3)}, \ldots\right)\Psi = E\mathbf{s}^{(0)}\Psi \qquad (4)$$

where $\mathbf{s}^{(1)}$, $\mathbf{s}^{(2)}$, . . . are matrix-operators constructed so that their characteristic values are the characteristic values of the $s^{(1)}$, $s^{(2)}$, . . . and where the meaning of $\mathbf{s}^{(1)}\Psi$ is given by

$$(\mathbf{s}^{(1)}\Psi)_\alpha = \sum_{\sigma = \alpha, \beta, \gamma, \delta} s^{(1)}_{\alpha\sigma}\psi_\sigma \qquad (5)$$

the symbols α, β, γ, δ referring to the rows and columns in the matrix $\mathbf{s}^{(1)}$. The element $s^{(1)}_{\alpha\sigma}$ is therefore the element of the matrix $\mathbf{s}^{(1)}$ belonging to the αth row and to the σth column. The matrix $\mathbf{s}^{(0)}$ is a unit matrix having the same number of rows and columns as $\mathbf{s}^{(1)}$, $\mathbf{s}^{(2)}$, . . . Having obtained solutions for (4), i.e., having found the characteristic E's and the ψ_σ belonging to these E's, Pauli gives a general way of expressing the matrix-elements belonging to the quantities $s^{(1)}$, $s^{(2)}$, . . . Thus let the characteristic E's be E_n and the corresponding ψ_σ be $\psi_{\sigma,n}$. Then the matrix-elements of $s^{(k)}$ are given by

$$S^{(k)}_{nm} = \int d^{(k)}_{nm}\, dq \qquad (6)$$

where

$$d^{(k)}_{nm} = \sum_{\sigma,\tau}\psi^*_{\sigma,n}\, s^{(k)}_{\sigma\tau}\psi_{\tau,m}, \quad (\sigma, \tau = \alpha, \beta, \gamma, \ldots). \qquad (7)$$

We may say that the density of $s^{(k)}$ in the q-space is represented by the Hermitian quadratic form, the matrix of which is the operator matrix and the variables of which are ψ^*, ψ. At the same time the probability of finding the electron in unit volume at q is determined by matrix-elements

$$d^{(0)}_{nm} = \sum\psi^*_{\sigma,n}\, s^{(0)}_{\sigma\tau}\psi_{\tau,m} = \sum\psi^*_{\sigma,n}\psi_{\sigma,m}. \qquad (8)$$

This gives us an immediate means of testing the supposition that α_1, α_2, α_3 are operational representations of $-(\dot{x}/c, \dot{y}/c, \dot{z}/c)$ because if this be true $+ ec\alpha_1$, $+ ec\alpha_2$, $+ ec\alpha_3$ should represent the components of current density while $-e$l. should be the charge density. Dirac's α's are readily seen to be

$$\alpha_1 = \begin{vmatrix} 0 & 0 & 0 & 1 \\ 0 & 0 & 1 & 0 \\ 0 & 1 & 0 & 0 \\ 1 & 0 & 0 & 0 \end{vmatrix}, \quad \alpha_2 = \begin{vmatrix} 0 & 0 & 0 & -i \\ 0 & 0 & i & 0 \\ 0 & -i & 0 & 0 \\ i & 0 & 0 & 0 \end{vmatrix},$$

$$\alpha_3 = \begin{vmatrix} 0 & 0 & 1 & 0 \\ 0 & 0 & 0 & -1 \\ 1 & 0 & 0 & 0 \\ 0 & -1 & 0 & 0 \end{vmatrix}, \quad \alpha_4 = \begin{vmatrix} 1 & 0 & 0 & 0 \\ 0 & 1 & 0 & 0 \\ 0 & 0 & -1 & 0 \\ 0 & 0 & 0 & -1 \end{vmatrix}.$$

Therefore,

$$\begin{aligned}
\rho &= -e(\psi_1\psi_1^* + \psi_2\psi_2^* + \psi_3\psi_3^* + \psi_4\psi_4^*) = -e\,\Psi^*(1\cdot\Psi) \\
J_1 &= +ec(\psi_1^*\psi_4 + \psi_2^*\psi_3 + \psi_3^*\psi_2 + \psi_4^*\psi_1) = ec\,\Psi^*(\alpha_1\Psi) \\
J_2 &= ec(-i\,\psi_1^*\psi_4 + i\,\psi_2^*\psi_3 - i\,\psi_3^*\psi_2 + i\,\psi_4^*\psi_1) = ec\,\Psi^*(\alpha_2\Psi) \\
J_3 &= ec(\psi_1^*\psi_3 - \psi_2^*\psi_4 + \psi_3^*\psi_1 - \psi_4^*\psi_2) = ec\,\Psi^*(\alpha_3\Psi). \qquad (9)
\end{aligned}$$

These are exactly the expressions found by Darwin[3] and to within a constant factor are also the expressions derived by Dirac[4] in the form

$$\frac{\varphi\gamma_0\chi}{c},\ -\varphi\gamma_1\chi,\ -\varphi\gamma_2\chi,\ -\varphi\gamma_3\chi$$

which for comparison should be transformed by letting $\varphi = \psi^*$, and returning from χ to ψ by $\chi = \rho_3\psi$.

The above method of deriving the current four-vector is simpler than Darwin's and seems to be of interest mainly as an illustration of the fact that (2) may be looked at as a quantum mechanical version of (1). On the same basis we would expect

$$-\sqrt{1-\beta^2} = \psi_1^*\psi_1 + \psi_2^*\psi_2 - \psi_3^*\psi_3 - \psi_4^*\psi_4$$

as the volume density of $-\sqrt{1-\beta^2}$.

On forming the characteristic determinants for the matrices α_1, α_2, α_3, α_4 we find that all of them are of the form

$$(\lambda^2 - 1)^2 = 0 \qquad (10)$$

showing therefore that the only "possible" values of $\frac{\dot{x}}{c}, \frac{\dot{y}}{c}, \frac{\dot{z}}{c}, +\sqrt{1-\beta^2}$ are ± 1. The only "possible" values of $\dot{x}$, $\dot{y}$, $\dot{z}$ are therefore $\pm c$. At first sight this looks absurd because it implies that the only possible measured velocity of an electron is the velocity of light. Any other velocity has to be thought of as the statistical result of the superposition of $+c$ and $-c$. This, however, is not different from the way in which in Pauli's theory the angular momentum of the electron could be only $\pm \frac{h}{4\pi}$. Just as in Pauli's case it may be shown here that

$$\alpha_1 \cos\epsilon_1 + \alpha_2 \cos\epsilon_2 + \alpha_3 \cos\epsilon_3,$$

where $(\cos\epsilon_1, \cos\epsilon_2, \cos\epsilon_3)$ are three direction cosines, has the characteristic values ± 1 so that the apparently contradictory statement that $\dot{x}$, $\dot{y}$, $\dot{z}$ have characteristic values $\pm c$ does not make it impossible, and in fact makes it even necessary to consider $\dot{x}\cos\epsilon_1 + \dot{y}\cos\epsilon_2 + \dot{z}\cos\epsilon_3$ as also having the same characteristic values $\pm c$. This statement is only a special case of the following. The characteristic determinant of

$$P_1\alpha_1 + P_2\alpha_2 + P_3\alpha_3 + P_4\alpha_4$$

is

$$(P_1^2 + P_2^2 + P_3^2 + P_4^2 - \lambda^2)^2 = 0,$$

which may be worked out by a somewhat lengthy expansion. The characteristic values of $\sum_1^4 P_n\alpha_n$ are therefore $\pm\sqrt{\sum_1^4 P_n^2}$. If we specialize and make $P_1 = \frac{mv_x}{\sqrt{1-\beta^2}}, \ldots, P_4 = mc$ we obtain $\lambda = \pm\frac{mc}{\sqrt{1-\beta^2}}$ which is another way of saying that for a free electron the two analytically possible energy values are $\pm\frac{mc^2}{\sqrt{1-\beta^2}} = \lambda c$.

In Pauli's spinning-electron theory the interpretation of $s_1 \cos \epsilon_1 + s_2 \cos \epsilon_2 + s_3 \cos \epsilon_2$ having characteristic values ± 1 is made clear by the statement that if we were to measure the electron spin in the direction ($\cos \epsilon_1$, $\cos \epsilon_2$, $\cos \epsilon_3$) we would have to apply a magnetic field in that direction and, therefore, we would in the process of measurement itself orient the electron spin either along or oppositely to the field. It is in this sense of being experimentally accessible that the electron spin in any direction has values ± 1. In Pauli's presentation the empirical impossibility of obtaining any other values can form the starting point. We must ask as to whether the same is true in Dirac's case? Is it possible to see *a priori* that the characteristic values of $\frac{\dot{x}}{c}, \frac{\dot{y}}{c}, \frac{\dot{z}}{c}, \sqrt{1-\beta^2}$ in (1) are all ± 1? If so, we should like to consider (2) as derived from (1).

In the ordinary considerations of special relativity we are used to assign simultaneously values to $\dot{x}/c$, $\dot{y}/c$, $\dot{z}/c$ and we are used to think of these as taking on all possible values between -1 and $+1$. The measurements which are supposed to yield these values imply our ability of knowing the world-line of the electron, i.e., its position at any time. It is clearly impossible to use such considerations in the new mechanics. We have no way of discussing simultaneously position and velocity on account of Heisenberg's uncertainty relation. We may try however to discuss the velocity from the point of view of (1) from a knowledge of the energy. As long as (1) contains explicitly all four quantities $\left(\frac{\dot{x}}{c}, \frac{\dot{y}}{c}, \frac{\dot{z}}{c}, \sqrt{1-\beta^2}\right)$ we cannot infer the value of either. For a free electron the above four quantities are multiplied by p_x, p_y, p_z, mc, respectively. If we wish to ascertain $\dot{x}/c$ we must make p_y, p_z, mc equal to zero. This is impossible unless we make $m = 0$. Thus it is impossible to ascertain the velocity by means of the energy unless the mass is made to vanish. However, p_x, p_y, p_z can conceivably be all made $= 0$ and then $\sqrt{1-\beta^2}$ can have only the values ± 1.

If we make $m = 0$ the energy $H = \dot{x}p_x$. Since $\dot{x}$ can be only $\pm c$ we obtain the relation between the energy and the momentum of the light-quantum. In the case of the light-quantum the velocity is always c. We cannot measure its velocity except in the direction of propagation because a real measurement of the velocity of a light-quantum involves only two points: the point where it has been emitted and the point where it has been absorbed. Resolution of the velocity in components is obviously a fiction.

If we were to try to measure the velocity of an electron directly, the simplest experiment we could devise would consist in arranging two thin fluorescent screens which the electron (β-particle) would pierce in succession. The screens could conceivably be arranged *in vacuo* a long distance apart. Two observers would locate the spots on the screens and note the time of their appearance. If the precision of locating the spots will be made large the fluorescence will have to consist of large quanta on account of diffraction phenomena as in Heisenberg's γ-ray microscope. It is necessary to locate the spots accurately if a number is to be assigned to the final velocity. The large quanta necessary for this measurement will introduce an uncertainty in the velocity. Only if the speed of the electron is that of light will there be a negligible effect on the velocity because the relativity mass then is infinite. A similar reasoning applies to any attempt of directly observing the electron during its motion by means of microscopes. If the speed of the electron is that of light, we can theoretically assign a value to the speed. However, the elementary measurement gives the velocity only in the direction of observation—not the three components. For any physical system we believe that there are possibilities of motion in all possible directions on account of the spreading of the wave-packet. We cannot talk therefore of the velocity being definitely in one direction. We may only measure velocities in different directions and count statistically the number of observations or what we usually call the number of particles moving along OX or along OY. We see therefore that from the point of view of new mechanics we must regard $\dot{x}/c, \dot{y}/c, \dot{z}/c$ as having characteristic values ± 1.

It may be mentioned also that according to Gordon[5] the radiation in the case of the Compton-effect is really due to a $\psi\psi^*$ wave moving with the velocity of light. Similarly, the writer[6] has shown that if the motion of the center of gravity of an atom is taken into account the emission takes place only by means of unidirectional quanta due to $\psi\psi^*$ waves moving with the velocity of light. We may say therefore that the really observable radiation effects are due to electronic charge densities moving with the speed of light.

We should like therefore to look at (1) as the proper equation to form a starting point for the derivation of (2), and we should like to add to the

three explicitly stated premises of Dirac a fourth premise, namely, that the characteristic values of $\frac{\dot{x}}{c}, \frac{\dot{y}}{c}, \frac{\dot{z}}{c}, \sqrt{1-\beta^2}$ are ± 1.

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REGULARITIES EXHIBITED BETWEEN CERTAIN MULTIPLETS FOR ELEMENTS IN THE SECOND LONG PERIOD[1]

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If, for a sequence of iso-electronic systems starting with any element in the periodic table, the energy levels representing any of the possible electron configurations be plotted on a Moseley type of diagram, the lines connecting points for corresponding terms of each successive element will be very nearly straight lines. Furthermore, it is found that the radiated frequencies resulting from those electron transitions involving no change in total quantum number (which in some cases involve more than a hundred radiated lines) are displaced to higher and higher frequencies by very nearly a constant value. These general rules, the *regular displacement of multiple levels and of multiplets* which were found to hold so well for sequences of iso-electronic systems in the first long period,[1] have now been extended to the elements in the second long period.

In the so-called "*iron group*" of elements most of the strong lines in the various spectra are the result of the electron transitions $4p$ to $4s$ in the presence of 0, 1, 2, 3. . . .10, $3d$ electrons, whereas, in the second long period the transitions become $5p$ to $5s$ in the presence of 0, 1, 2, 3 . . . 10, $4d$ electrons.

In general the electron transitions $d^{n-1}\,p$ to $d^{n-1}s$, where n is the number of extra nuclear electrons in the atom or ion in any state of ionization in excess of that in the neutral atom of the next preceding rare gas, involves so many radiated lines that in order to represent the position in the spectrum of each electron transition it is desirable to select a single line out of all those radiated.

The wave numbers given in table 1 and shown graphically in figure 1

TABLE 1

REGULAR DISPLACEMENT OF MULTIPLETS BY SUCCESSIVE ADDITION OF 4*d* ELECTRONS

DOUBLETS																			
$^2S_1-{}^2P_2$																			
$s-p$		TRIPLETS																	
Rb I		$^3D_3-{}^3F_4$																	
12816.5																			
11700.2		$ds-dp$		QUARTETS															
Sr II		Sr I		$^4F_5-{}^4G_6$															
24516.7	8912	**15604.3**																	
10971.3		11340.0		d^2s-d^2p		QUINTETS													
Yt III		Yt II		Yt I		$^5F_5-{}^5G_6$													
35488.0	8544	**26944.3**	8656	**18288.3**															
10713.5		11203.9		11184.8		d^3s-d^3p		SEXTETS											
Zr IV		Zr III		Zr II		Zr I		$^6D_5-{}^6F_6$											
46201.5	8053	**38148.2**	8675	**29473.1**	8147	**21326.0**		d^4s-d^4p											
		11036.6		11213.9		10983.1		Cb I		SEPTETS									
		Cb IV		Cb III		Cb II		**24629.8**		$^7S_3-{}^7P_4$									
		49184.8	8498	**40687.0**	8378	**32309.1**	7679	10869.1											
				11147.4		11250.8		Mo II		d^5s-d^5p	SEXTETS								
				Mo IV		Mo III		**35498.9**		Mo I	$^6D_5-{}^6F_6$								
				51834.4	8274	**43559.9**	8061	Ma III	9180	**26319.3**	d^6s-d^6p		QUINTETS						
						Ma IV				Ma II	Ma I		$^5F_5-{}^5G_6$						
								Ru IV					d^7s-d^7p		QUARTETS				
										Ru III	Ru II		Ru I		$^4F_5-{}^4G_6$				
											40696.3	12124	**28571.8**						
													13758.0		d^8s-d^8p		TRIPLETS		
										Rh IV	Rh III		Rh II		Rh I		$^3D_3-{}^3F_4$		
													42329.8	13225	**29104.6**				
															14425.7		d^9s-d^9p		DOUBLETS
											Pd IV		Pd III		Pd II		Pd I		$^2S_1-{}^2P_2$
															43530.3	14166	**29363.8**		
															13588.7		15137.4		$d^{10}s-d^{10}p$
													Ag IV		Ag III		Ag II		Ag I
															57119.0	12618	**44501.2**	14028	**30473**
																	14077.3		16146
															Cd IV		Cd III		Cd II
																	58578.5	11959	**46619**
																	13794.5		14908
																	In IV		In III
																	72373.0	10846	**61527**
																	13773.7		14550
																	Sn V		Sn IV
																	86146.7	10070	**76077**

are chosen in the following way. In the one and eleven electron systems, columns one and eleven, the strongest line of the principal doublet $^2S_1 - {}^2P_2$ is chosen to represent the electron transition p to s. For the two and

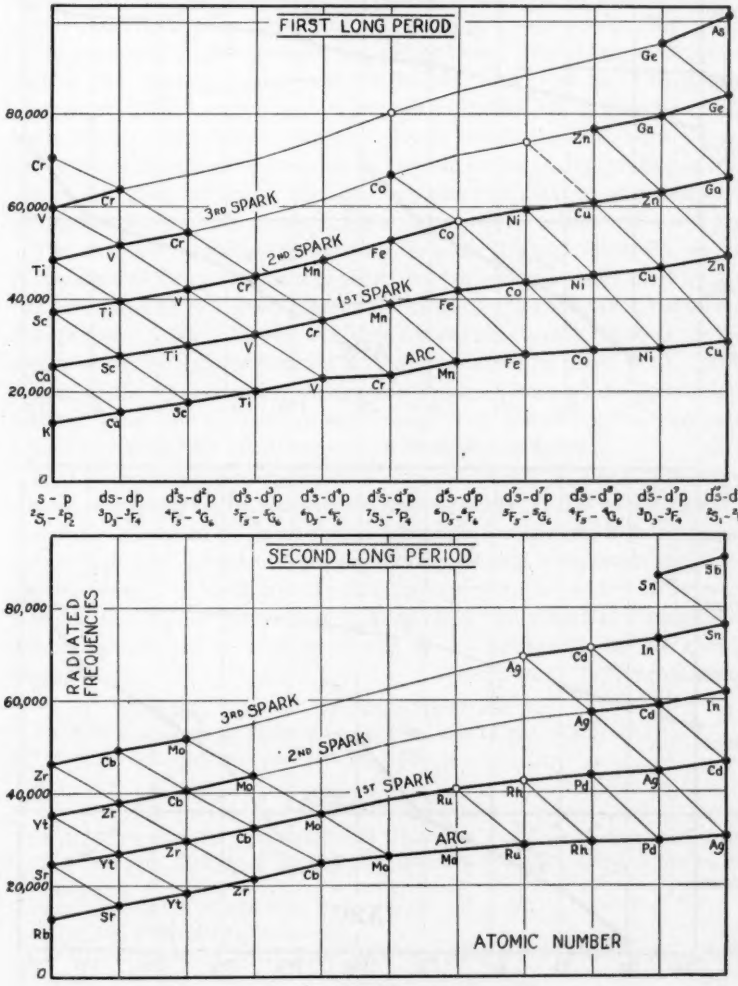

FIGURE 1

Transitions in iso-electronic sequences ($d^{n-1}p \rightarrow d^{n-1}s$).

ten electron systems, columns two and ten, the strongest line $^3D_3 - {}^3F_4$ is chosen to represent the transitions dp to ds and d^9p to d^9s, respectively.

Similarly, for the three and nine electron systems the line $^4F_5 - {}^4G_6$ is chosen to represent the transitions d^2p to d^2s and d^8p to d^8s, respectively.

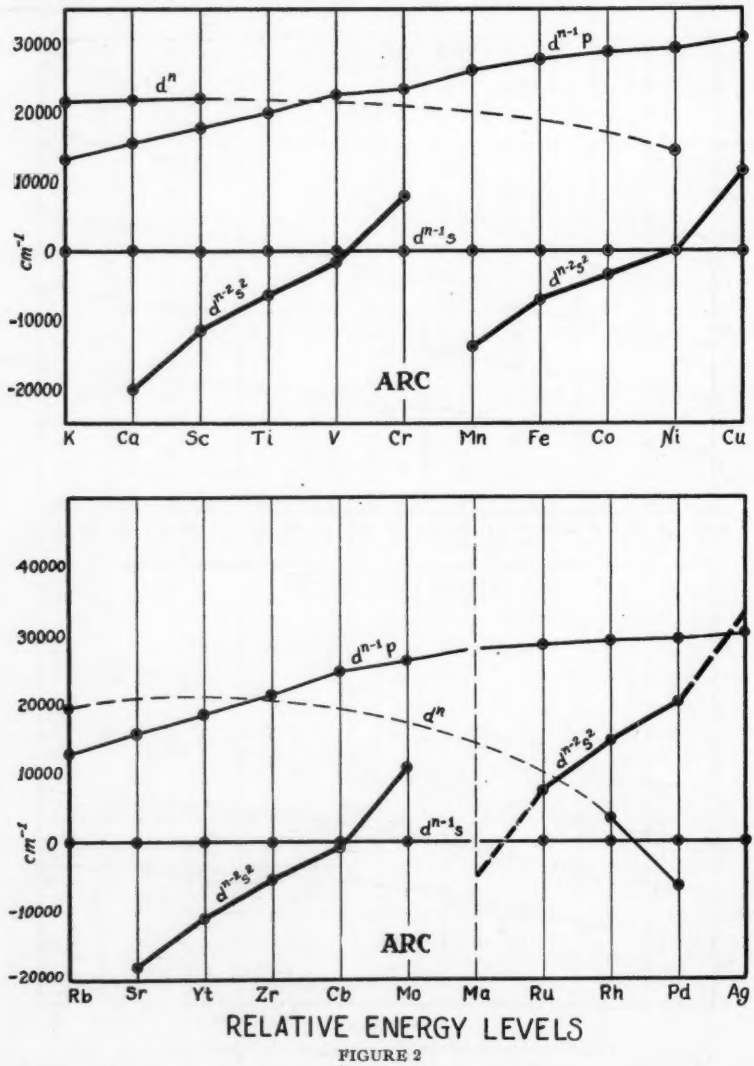

FIGURE 2

In like manner this process is repeated for each of the remaining sequences of iso-electronic systems, choosing each time the transition which

takes place between two levels involving the highest R, L and J values. The diagram for elements of the first long period as it appears in figure 1, which includes several extensions to that given in a previous report,[2] along with the corresponding figure below for elements of the second long period offers some very interesting and valuable comparisons. The points along any vertical line represent the almost linear progression of frequency with atomic number in a sequence of iso-electronic systems. With these diagrams extended as far as they have been further extrapolations can be made with considerable accuracy. For a number of the points given above the radiated lines were predicted within one or two angstroms of their observed values, indicating that this is a powerful method of attack upon the spectra arising from atoms in higher states of ionization.

The recognized similarities between both the arc and the spark spectra of the corresponding elements in these two periods have been used by several investigators to unravel some of the more complex spectra in the second long period. With data now available for the arc spectra of ten of the elements in the second long period a comparison can be made with the arc spectra of the corresponding elements in the first long period. Similarities between these two periods are well brought out (following a scheme suggested by Russell[3] for the *iron group* of elements) in figure 2.

Here the electron configurations $d^{n-2}s^2$, $d^{n-1}s$, $d^{n-1}p$, and d^n are represented, where known, by plotting the lowest energy level of each configuration with respect to $d^{n-1}s$ as zero. Although the spectra of masurium is not yet known it is evident from the two figures that a similar break in the relative energies of binding of the different configuration occurs at the same place in each period. In passing through these two periods of elements the decreasing *energies* of binding of the $d^{n-2}s^2$ configurations are clearly brought out.

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ANGULAR SCATTERING OF ELECTRONS IN HYDROGEN AND HELIUM

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In view of the recent work which has been done by Davisson and Germer,[1] G. P. Thomson,[2] and others in investigating the angular scattering of electrons by crystals, and the work of E. G. Dymond[3] in extending these investigations to the scattering of electrons by helium, it was thought worthwhile to see if similar results could be obtained for this scattering by other monatomic and diatomic gases. The phenomena observed when electrons are scattered by crystals are susceptible of explanation in a very satisfactory way on the wave mechanics hypothesis, but the theory is less fully developed for the case of gases and the results obtained by Dymond for scattering in helium have so far met with no adequate explanation. However, selective angular scattering might conceivably be expected in a monatomic gas. In this case it might be supposed that atomic hydrogen would also give rise to similar phenomena, and in view of its greater simplicity an explanation would present less serious mathematical difficulties. Hence, the following work was undertaken primarily to investigate the possibility of selective angular scattering in atomic hydrogen. Molecular hydrogen was also used though there was less reason to expect the phenomena in a diatomic gas. Finally, the experiments performed by Dymond in helium were repeated under as nearly similar conditions as possible.

The apparatus used is shown in figure 1. The scattering chamber consisted of a glass bulb about ten centimeters in diameter. A large ground glass stopper mounted vertically through a mercury seal carried the electron gun, *G*. This consisted of a tungsten filament mounted behind two collimating slits about a quarter of a millimeter wide and a centimeter and a half apart. By means of the ground glass stopper this could be rotated through nearly a complete circle. The angular setting could be read by means of a pointer attached rigidly to the stopper carrying the gun and an angular scale attached to the bulb. The front slit of the gun

was about two and a half centimeters from the center of the bulb. As an electrometer was not available the electrons could not be analyzed magnetically and a scheme similar to that used by Davisson and Germer had to be adopted. A brass tube carrying a slit S_1 about a tenth of a millimeter wide projected through a wax joint to within a few millimeters of the center

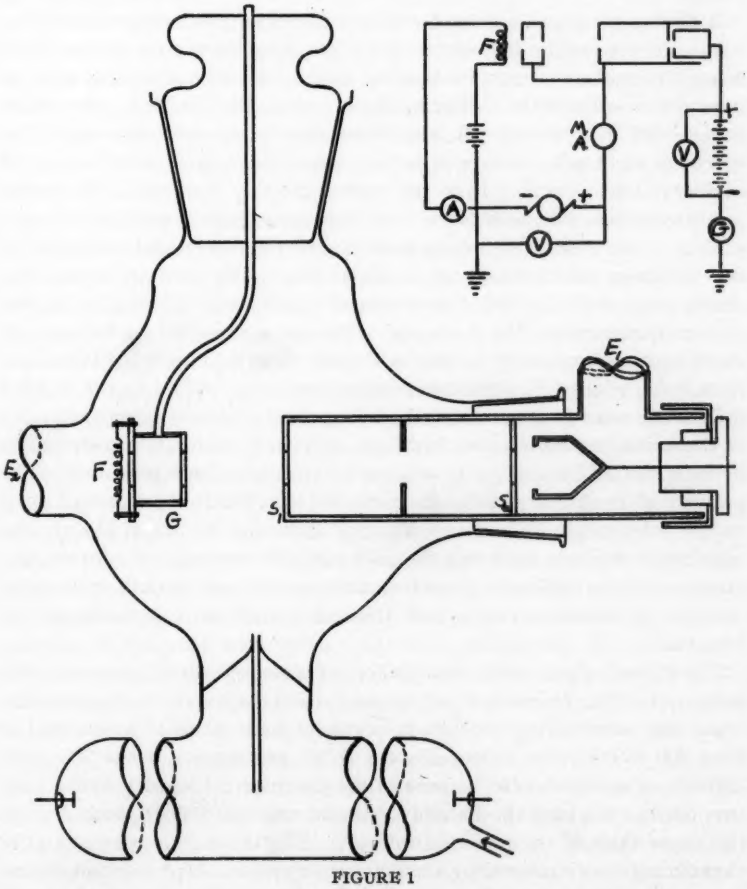

FIGURE 1

of the bulb. About four centimeters farther in the tube was placed a collimating slit, S_2, and immediately behind this an insulating plug supported a Faraday cylinder as shown. By varying the potential of the Faraday cylinder those electrons which had lost less than any given fraction of their energy could be collected. A diaphragm was mounted be-

tween S_1 and S_2 and a skeleton partition supported S_2 so that little resistance was offered to the flow of gas in the brass tube. A continuous flow method was used and the pressure in the brass tube could be kept lower than that in the scattering chamber by means of diffusion pumps evacuating through E_1. The other exit E_2 was connected to a second set of diffusion pumps.

A discharge tube about a meter and a quarter long was mounted with its center directly below the scattering bulb. A capillary tube of one millimeter bore and six or eight centimeters long led from the discharge tube up toward the center of the scattering bulb. When the discharge tube which was excited by a 25,000 volt transformer was in operation the many line spectrum was hardly detectable in the region immediately surrounding the capillary tube. Judging from the reports of other workers under similar conditions there was probably a very large percentage of atomic hydrogen present. The hydrogen was generated electrolytically and admitted to the discharge tube through an artificial leak. The pressure in the discharge tube could be varied up to about a millimeter in order to get the proper conditions for the discharge. The pressure in the scattering bulb could be varied relatively to that in the discharge tube by using both exits E_1 and E_2, or only E_1. Pressures in the scattering bulb up to 5×10^{-2} millimeters were used. An ionization gauge (not shown) connected directly to the scattering bulb which had been previously calibrated in hydrogen by means of a Macleod gauge was used to measure these pressures. The pressure in the discharge tube was measured by a Macleod gauge connected to the inlet tube. When investigating molecular hydrogen exactly the same apparatus was used, but the discharge tube was not run. In the last experiments the hydrogen generator was removed and a tank containing commercial helium was attached through a charcoal tube immersed in liquid air.

The scheme of potentials finally adopted is also shown diagrammatically in figure 1. The filament, F, was grounded and the body of the gun and the brass tube surrounding the Faraday cylinder were raised to a potential of from 200 to 800 volts by means of a D. C. generator. Below 200 volts difficulty was experienced because of the diminished intensity of the electron current reaching the Faraday cylinder, and 800 volts appeared to be the upper limit of the region of interest. The thermionic current to the electron gun was measured by a milliammeter and was kept constant during a run at a value of from five to ten milliamperes. The potential between the filament and the Faraday cylinder was always (except for various tests) kept at one-tenth that existing between the filament and the body of the electron gun. So that only those electrons which had lost less than one-tenth of their original energy were able to reach the collector and be recorded. Other arrangements of the potentials differing in various re-

spects from the one just described were experimented with, but the above arrangement was decided on as giving the most satisfactory conditions. Also during the first part of the experiments immediately to be described the scattering chamber was surrounded by a shielding screen of copper gauze at the same potential as the electron gun and the tube surrounding the Faraday cylinder.

Molecular hydrogen was first introduced into the apparatus, and the peaks in the galvanometer current which were found to appear as the electron gun was moved around in a circle from its zero position were investigated under various conditions of pressure and of electron speed, as given by the potential difference existing between the filament and the slits of the gun. The zero position was determined quite accurately by the very sharp maximum found at any pressure and at any voltage used when the gun pointed directly into the collector. The voltages used were all too high to show any appreciable small angle scattering in either hydrogen or helium and hence as the gun was moved away from its zero position the current to the Faraday cylinder dropped practically to zero in two degrees or less. At high pressures when the mean free path was approximately from one-fifth to one-tenth the diameter of the bulb the peaks were rather low and broad. This was due very probably to the fact that the primary effect under observation was interfered with by subsequent collisions of the electrons. Under any of the conditions used only one peak appeared. At speeds corresponding to 800 volts and at the highest pressure used it appeared at about 52 degrees. As the voltage was decreased to 200 the peak moved slowly but continuously down to about 36 degrees. At lower pressures the behavior of the peak with voltage was of the same character but the actual amount of the variation became less and less down to a pressure of about 1×10^{-3} millimeters. Below this pressure the angular variation of the peak with voltage was reversed slightly, the peak corresponding to 800 volts appearing at a slightly smaller angle than that obtained at 200 volts. The peak became higher and sharper as the pressure was decreased. Below the pressure of 1×10^{-3} the peak became very high and narrow being of the order of one degree in width. But when all the gas was removed from the apparatus the peak did not disappear. The intensity of this peak represented under various circumstances from one-tenth to one-quarter the number of electrons which were found to reach the Faraday cylinder when the gun was pointing directly into the collector. However, the sensitivity of the galvanometer used was such that any peaks of over one-thousandth the intensity of the original beam could easily have been detected.

After this work the discharge was run under conditions such that the hydrogen existing in the region where the scattering took place was probably to a very large per cent in the atomic condition. The same procedure

outlined above was repeated. The peak was found to be present and to behave in exactly the same way within the limits of error. No new peaks were observed. As this peak was found to be present, though very narrow, even when the pressure was as low as 1×10^{-5} millimeters it could not reasonably be due to angular scattering from the gas. A possible explanation was thought of in the charging up of the glass walls of the scattering bulb opposite the electron gun and consequent deflection of the electron stream by the electrostatic charge.

In order to test this possibility the electron gun was removed and the inside of the scattering chamber was given a heavy coating of magnesium by vaporization from a filament. Some experiments showed that this magnesium layer was of high conductivity and in electrical contact with the tube surrounding the Faraday cylinder. Consequently, in the following work it was at the same potential as this tube and the body of the electron gun. The electron gun was then returned to position and the above experiments were repeated using the same procedure, the only altered condition being the presence of the shielding layer of magnesium on the inside of the scattering bulb. Under these conditions no peaks whatever were observed at any pressure or voltage in either molecular or atomic hydrogen. As has been mentioned above any peaks equal in magnitude to one-thousandth of the original beam could have been detected. In the course of several weeks after the magnesium coating had worn off in spots under the influence of the hot filament small peaks began to appear at various angles. These remained when there was no gas in the apparatus, showing fairly conclusively that the peaks observed were due to electrostatic charges on the inside of the scattering bulb.

In the light of these negative results it was thought to be of interest to repeat Dymond's experiments as nearly as possible in the present apparatus. Helium was introduced into the apparatus and investigated in an exactly similar way as that which has been described for hydrogen. In the presence of the film of magnesium no peaks were observed. As the film wore off certain peaks appeared which behaved with pressure exactly as those described for hydrogen. These did not disappear when the pressure was reduced to the lowest possible value, which was approximately 1×10^{-6} millimeters of mercury.

The results may briefly be summed up as follows. No favored angles for electron scattering from hydrogen or from helium were observed, and in the case of helium the results obtained by Dymond were not able to be reproduced.

In conclusion it is a pleasure to thank Mr. Arnquist for his assistance in taking readings, the California Institute of Technology for the facilities extended for the work, and the National Research Council for its support which made the work possible.

* NATIONAL RESEARCH FELLOW.

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THERMODYNAMICS BASED ON STATISTICS. I

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Many attempts have been made to deduce thermodynamics from statistical mechanics, and no one can doubt the intimate relationship or even the complete identity of the two sciences. Nevertheless, it has not hitherto been found possible to proceed by a single path unambiguously from simple statistical assumptions to the laws of thermodynamics. This we hope to have accomplished in this paper and the following.

When the Second Law of Thermodynamics was first accepted, it was regarded as an exact law of universal validity. The concept of entropy which Clausius associated so intimately with his statement of the second law, was regarded as a quantity which could be defined, or at least the changes in which could be defined, without the slightest ambiguity. It was Gibbs who first suggested the idea, which was developed with so much acumen by Boltzmann, that entropy is related to a probability and that the second law expresses, not an infallible prediction, but a reasonable expectation. Indeed, Clausius' statement that an isolated system proceeds in a uniform direction toward a state of maximum entropy, seems, according to modern views, to be unsatisfactory, for we believe that any particular (microscopic) state of an isolated system will in endless time recur over and over.

Boltzmann, following Clausius, considered entropy to be defined only to an arbitrary constant, and related the difference in entropy between two states of a system to their relative probability. An enormous advance was made by Planck who proposed to determine the absolute entropy as a quantity, which, for every realizable system, must always be positive (third law of thermodynamics). He related this absolute entropy, not to the probability of a system, but to the total number of its possibilities. This view of Planck has been the basis of all recent efforts to find the statistical basis of thermodynamics, and while these have led to many differences of opinion, and of interpretation, we believe it is now possible to derive the second law of thermodynamics in an exact form and to obtain

unambiguous definitions of the correlated quantities, such as entropy, temperature, and pressure, from simple statistical principles.

Fundamental Ideas.—In discussing any thermodynamic system, it is necessary to agree in advance as to whether we shall consider every conceivable change which may occur within the system or only certain specified changes, while the others may be said to be (absolutely) *inhibited*. The former method is more general, but the latter is usually required for reasons of convenience or because of the limitations of our knowledge. If, at ordinary temperatures, we are dealing with the properties of a gaseous mixture of hydrogen, water, and oxygen, the chemical combination of hydrogen and oxygen, in the absence of a catalyst, is so rare an occurrence as to be ignored, and we may in our thought consider the process as completely inhibited.

A given system is found to contain various molecular or atomic species, some of which, however, subject to the inhibitions which have been imposed, are derivable from the others. There is a minimum number of these species from which all may be derived, and a set of such species comprising the minimum number is called a set of independent constituents. In the case just cited, the number of independent constituents is 2 when the hydrogen and oxygen are allowed to combine, but is 3 when this process is inhibited. In all the simpler problems of thermodynamics a system may be said to be completely defined when we know the energy, the volume, and the amount of each species of a set of independent constituents. It is only such systems that we are going to consider.

Let us turn now to the statistical view of the problem. At one time in the development of statistical mechanics it was considered necessary to define the instantaneous microscopic state of a system by telling exactly the position, the momentum, and every other mechanically significant property of each particle. Such a detailed description seems now to be of doubtful feasibility and, moreover, seems unnecessary.

All the statements regarding positions, momenta, quantum numbers of rotation, of vibration, and so on, constitute a manifold or field of specifications which may be conveniently partitioned into a number of regions. For example, we could divide the field crudely into two regions, one of which comprises all molecules with individual gross energies lying below, the other all molecules with energies lying above, a certain value. Again, we might set up smaller regions such as one containing all molecules whose positions lie between x and $x + \Delta x$, between y and $y + \Delta y$, and between z and $z + \Delta z$, whose momenta are comprised in the range Δp_x, Δp_y, Δp_z, and whose other specifications are similarly comprised within fixed limits.

After we have decided upon such a convenient partition into regions, we shall deem it sufficient to describe the *detailed state* merely by specifying

the number of molecules of each independent constituent which are contained in each region, *without attempting to distinguish otherwise between different molecules of the same species* and without paying any attention to the absolute or relative positions of the molecules within any one region.

Equilibrium.—Two systems, or two parts of a system, may be said to be in equilibrium with each other if, when left in contact for indefinite time, there is no average change in any of the properties of either system.

If certain processes are inhibited then we may speak of equilibrium with respect to the remaining processes which are allowed. Thus if two systems are separated by a rigid wall, which permits no change of volume of one at the expense of the other, and which permits no transfer of material, but only a flow of heat, the two systems are said to be in thermal equilibrium when the distribution of energy is the same as the average distribution over an infinite time.

Let us consider a system for which the total manifold of specifications has been partitioned into finite regions, and let this system be divided into two parts J and K, such that each region may be said to belong entirely to J or entirely to K, with the same order of accuracy as the definition of the regions themselves. The division may be a spacial one, or J may comprise all regions in which particles have energies below, and K all above, a certain value, or J may include all particles of one kind, K of another. Indeed, we may make any sort of division which is physically or mentally significant. Since now the regions are of finite extent, and since the total energy and the total number of particles (of each constituent) are fixed, there is a finite number of detailed states, as we have defined them, which the system as a whole can assume.

The total number of detailed states may be classified by the distribution of material, energy, etc., between J and K. If we specify that J shall contain a certain number of particles of each constituent, a certain number of (arbitrarily chosen) units of energy, etc., we thus define a definite distribution which may comprise a large number of individual detailed states.

For reasons of convenience, we are now going to modify our definition of equilibrium by calling the equilibrium distribution, not the average over an indefinite number of observations of all the several distributions, but the distribution which is most often observed. While there is a logical difference between these definitions, they may, as we shall see presently, be regarded as practically synonymous except in very extraordinary cases which will need to be discussed separately.

Returning to our system J, K, in which the total possible number of detailed states may be designated by Ω we may find by a vast number of observations that some states are observed more often than others. If we call w_s the fraction of all the observations that give the detailed state

s, this is also the chance that that state will be found in a single observation. Hence, for the totality of states,

$$\sum w_s = 1. \tag{1}$$

Of all the states, Ω^d may represent the number that are possible with a given distribution d. The probability of finding this distribution is the sum of the probabilities of the individual states comprising this distribution, namely, $\sum w_s^d$, and this may, in turn, be replaced by $\overline{w}^d\Omega^d$ where $\overline{w}^d$, being defined by this identity, may be called the average probability of all the states in the given distribution. This expression will be greatest for some one distribution, which must be, according to our definition, the equilibrium distribution. We may therefore write for the equilibrium distribution,

$$\sum w_s^d = \overline{w}^d\Omega^d = \text{max.} \tag{2}$$

Each detailed state is described by giving the conditions in each region belonging to J, and in each region belonging to K, and may therefore be regarded as a combination of a J-state and a K-state. If Ω_J^d and Ω_K^d represent the numbers of these special states which are compatible with a given distribution, then since each of these special states can be combined with any one of the special states of the other system,

$$\Omega^d = \Omega_J^d\Omega_K^d. \tag{3}$$

It may be possible that we could have varied the original partition into regions so that all the individual detailed states would be found equally often. In that case, all of the individual values w_s would be equal to one another and also equal to any one of their averages. With such a partition into regions, the condition for the equilibrium distribution is that Ω^d or $\Omega_J^d\Omega_K^d$ is a maximum. Hence, we may write for any variation of distribution,

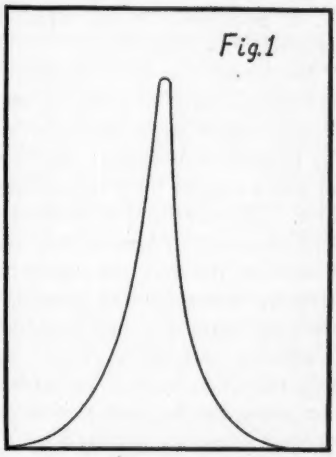
$$\delta\Omega^d = \delta(\Omega_J^d\Omega_K^d) = \Omega_K^d\delta\Omega_J^d + \Omega_J^d\delta\Omega_K^d = 0, \tag{4}$$

and, dividing by $\Omega_J^d\Omega_K^d$,

$$\delta(\log \Omega_J^d) + \delta(\log \Omega_K^d) = 0. \tag{5}$$

We may illustrate some of our previous remarks by means of figure 1. Consider the mere spacial distribution of particles between two flasks of nearly the same size. The abscissa, indicating the fraction of the particles in the first flask, thus determines the distribution. The ordinate represents (on a greatly reduced scale) the number of detailed states corresponding to each distribution. A curve of the type illustrated will then be obtained. However, the central protuberance is ordinarily exceedingly slender. If the number of regions chosen happens to be somewhat larger than the number of particles, then, even at an ordinate which is one-millionth of the

maximum ordinate, it will have only 10% of the whole width of the diagram with a thousand particles, 0.01% with a billion particles and the width continues to diminish with great rapidity as the number of particles increases. It becomes therefore increasingly difficult to distinguish between the two distributions (abscissae) of which one marks the maximum ordinate, and one divides the curve into two equal areas, thus corresponding to the two definitions of equilibrium which we have given. In fact, we know from experience that except in the very rare cases where fluctuations are noticeable that one measurement of the distribution at equilibrium is identical with any other such measurement, far within the limits of experimental error.



It is evident that Ω^d, the number of states at the equilibrium distribution, is always smaller and usually very much smaller than Ω, the total number of detailed states; but it must always be greater than the average number of states per distribution, which is Ω/D if D is the total number of possible distributions. That is,

$$\Omega > \Omega^d > \frac{\Omega}{D}, \tag{6}$$

or

$$\log \Omega > \log \Omega^d > \log \Omega - \log D, \tag{7}$$

or

$$1 > \frac{\log \Omega^d}{\log \Omega} > 1 - \frac{\log D}{\log \Omega}. \tag{8}$$

Now while $\log D$ increases with the size and complexity of a system, $\log \Omega$ usually increases so much faster that the last ratio rapidly approaches zero. In the illustration that we have just cited, when the number of particles is 10^9 the value of $\log D/\log \Omega$ is of the order of 10^{-8}. Therefore, as an asymptotic expression, and also as a very close approximation, except when we are dealing with extremely small numbers of particles and regions, we may write for the number of states at the equilibrium distribution,

$$\log \Omega^d = \log \Omega. \tag{9}$$

Furthermore, while we are dealing with this asymptotic or approximate character of some of our equations, let us point out that it was far from

necessary in deriving equation 4 to assume the probabilities of the several states and their various averages to be exactly the same. They might indeed vary over enormously wide limits provided only that the variations in any log w or in any log $\bar{w}$ is negligible compared to the variations in log Ω. In such case, the individual detailed states will be said to be of the same order of probability.

The Second Law of Thermodynamics.—We have discussed the possibility of finding a mode of partition into finite regions such that the individual detailed states are of the same order of probability. We shall now make the cardinal assumption: not only is this possible for every system, but for every system there is a natural mode of partition into regions of this kind. This partition is assumed to be unique in the following sense: it is unnecessary to assume that the natural mode of partition completely determines the sizes and shapes of the individual regions, but that it does uniquely determine the quantity which we are going to find to be of essential thermodynamic importance, namely, log Ω.

Whether this uniqueness is absolute for systems that are made indefinitely small, must for the moment be left unanswered. Another reservation must also be made; if we accept at the outset certain inhibitions, whether these are imposed by nature or by arbitrary choice, we must always abide by these inhibitions in determining log Ω. For example, there may be a natural restriction in some cases which does not allow two particles of the same kind to appear in the same region,[1] or we may arbitrarily agree to disregard the possibility that hydrogen molecules and oxygen molecules might combine to form water. Such a set of inhibitions not only redefines log Ω but may even modify the partition into regions.

It is our purpose to show that our assumption regarding the natural partition into regions *comprises within itself both the second and the third laws of thermodynamics*, and that from it we may obtain all of the equations of thermodynamics, as soon as we have learned how to make the natural partition into regions for any single system, for all values of the energy, the volume, and the number of particles.

In many cases the natural partition into regions is easy. Thus in a system of like molecules which have no energy except vibrational, it is only necessary to make every region contain just one distinct quantum state. On the other hand, other cases will be later discussed in which attention must be given less to the actual partition into regions than to the mode of partition.

The natural mode of partition must be regarded as pliable, so that if two isolated systems are brought together, which means that the inhibitions between them are removed, the natural modes of partition automatically adjust themselves, if necessary, so that the new detailed states of the combined system are all of equal order of probability.

The essential idea contained in our assumptions is one which would have appeared absurd before Planck introduced the quantum theory, and is still hard to accept in all its implications. It means that thermodynamic properties are determined with all possible exactness when the detailed specifications are given, not to an infinite, but to a finite degree of approximation. Conversely, however accurately the thermodynamic properties are measured, this will determine the possible mechanical states of the molecules only within finite limits. Such a statement, although perhaps it cannot be fully comprehended at present, is more readily accepted since the remarkable demonstration by Heisenberg[2] that similar finite regions of tolerance are inherent even in the equations of mechanics.

The proof that the assumptions so far made are alone sufficient for the derivation of the equations of thermodynamics will be given in the following paper.

[1] Such an inhibition leads to statistics of the Fermi type (*Zeits. Physik*, **36**, pp. 902–912 (1926)), while our assumptions for unrestricted systems will lead to equations which agree in the main with the statistics of Bose and Einstein (*Zeits. Physik*, **26**, pp. 178–181 (1924); *Ber., Berlin Akad.*, **24–25**, pp. 261–267 (1924); **26–27**, pp. 3–14 (1925)).

[2] W. Heisenberg, *Zeits. Physik*, **43**, 172 (1927).

THERMODYNAMICS BASED ON STATISTICS. II

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In the preceding paper,[1] we have assumed that for a system having a certain volume, energy, and number of particles the whole field of specifications which describe the states of the individual particles is naturally partitioned into regions in such manner as to give unique significance to a quantity written as $\log \Omega$, where Ω represents the total number of recognizably different ways in which the particles may be distributed among the regions. We have stated that this assumption includes within itself the second law of thermodynamics. This we shall now proceed to show.

The Entropy.—Let us define a quantity S by the equation,[2]

$$S = k \log \Omega, \tag{10}$$

where k is a constant factor (which will later be identified with the Boltzmann constant).

We shall further define the quantities T and P by the two equations,

$$\left(\frac{\partial S}{\partial E}\right)_V = \frac{1}{T}, \tag{11}$$

$$\left(\frac{\partial S}{\partial V}\right)_E = \frac{P}{T}, \tag{12}$$

where E is the energy and V the volume. Although not expressed in the equations, the number of particles in each case is taken as constant. Dividing the second equation by the first we find

$$\left(\frac{\partial E}{\partial V}\right)_S = -P. \tag{13}$$

Since these equations are identical in form with the essential equations of thermodynamics, it will be our task to show that S, T, and P are identical with the thermodynamic entropy, temperature, and pressure.

Before proceeding to the detailed proof, we may show at the outset certain obvious analogies. The entropy of two large identical systems joined together is the sum of their individual entropies, but this is also true of the quantity S, for if two systems J and K are identical in all respects they will be in equilibrium when joined together. Therefore, from equations (3) and (9) of our previous paper, $\log \Omega$ for the combined system is equal to $\log \Omega_J + \log \Omega_K$. Also, we may show a qualitative resemblance between T and the temperature, for if any two systems J and K are in thermal equilibrium, then by equation (5),

$$\left(\frac{\partial S_J}{\partial E}\right)_V \delta E_J + \left(\frac{\partial S_K}{\partial E}\right) \delta E_K = 0, \tag{14}$$

but since δE_J and δE_K must be equal and opposite in sign,

$$T_J = T_K. \tag{15}$$

Thus any two systems at the same temperature have the same T, and any system which is kept at constant temperature is kept at constant T.

The Mode of Partition into Regions for an Ideal Monatomic Gas.—Before proceeding further, we must know how to calculate Ω for some one type of system. We might choose a system of oscillators; or we might choose radiation in a Hohlraum, using either the black radiation as in classical radiation theory or the more extended radiation theory discussed recently by one of us.[3] Any one of these would have some advantage over the system that we actually choose—a choice dictated by the large part that the perfect gas has played in the development of classical thermodynamics.

We shall define an ideal monatomic gas as one in which the molecules have no energy except translational, and (for reasons which will

not become evident in this paper) in which the mean free path is large compared with the dimensions of the enclosure. The whole field of specifications is here a manifold of six dimensions which may be represented by a 6-dimensional space whose six coördinates are the coördinates of position, q_x, q_y, q_z, and of momentum, p_x, p_y, and p_z.

We shall now make the assumption that in this case the natural mode of partition is one which assigns to all of the regions in this 6-dimensional field the same 6-dimensional volume.

It may be well to point out that this assumption of partition into equal regions in no way implies a complete quantization of the gas in the sense, for example, that a molecule can have only specified momenta. It is true that the new wave mechanics indicate that only such specified momenta occur. The case, however, would presumably be quite different in the new mechanics if the walls of the enclosure acted as perfect reflectors for the molecules. Indeed it seems likely that we shall find, even in the calculation of entropy, that it makes a difference whether the gas molecules suffer elastic or inelastic collisions at the walls.

Although it is not necessary for our present purpose, we shall, in accord with many other scientists, take the 6-dimensional volume φ of each region as equal to the cube of the Planck constant h. We may regard φ as the product of the volume of the region in ordinary space by the volume of the region in the 3-dimensional momentum space, so that,

$$\Delta q_x \Delta q_y \Delta q_z \Delta p_x \Delta p_y \Delta p_z = \varphi = \varphi_q \varphi_p = h^3. \tag{16}$$

Let each region be regarded as occupying the whole volume V so that $V = \varphi_q$ and,

$$\varphi_p = \frac{h^3}{V}. \tag{17}$$

Concentrating our attention, then, upon the momentum space, we may number the regions, and the momentum and the energy of a particle in region r may be called p_r and $\epsilon_r = p_r^2/2m$, where m is the mass of the particle. A sphere of volume Φ_p, outside of which the regions are never occupied, has a radius $p_{max.}$ which is the momentum of one particle possessing the whole energy E, so that $E = p^2_{max.}/2m$.

The total number of detailed states is the total number of distinct ways in which we can place the particles in the regions, subject only to the conditions that the total number of particles N and the total energy E remain constant; that is,

$$\Sigma N_r = N; \quad \Sigma N_r \epsilon_r = E. \tag{18}$$

Now let the whole gas expand. This will cause an equal and uniform contraction in each φ_p; more regions will crowd into the sphere determined

by the constant radius, $p_{max.}$ If, however, we allow the energy to diminish as V increases, we may compress that sphere so that Φ_p maintains a constant ratio to φ_p. Since Φ_p is proportional to $p^3_{max.}$ and, therefore, to $E^{3/2}$, while φ_p is inversely proportional to V, the desired result may be accomplished by keeping $E^{3/2}V$ constant.

When this is done, we see that the only change in the picture is one of scale, every p_r remains proportional to $p_{max.}$, and every ϵ_r to E. The equations that determine the total number of detailed states are therefore identical. We thus reach the important conclusion that Ω and, therefore, S remain constant when $E^{3/2}V$ is constant. Or expressed in another way,

$$\left(\frac{\partial E}{\partial V}\right)_S = -\frac{2}{3}\frac{E}{V} \tag{19}$$

and with equation (13)

$$P = \frac{2}{3}\frac{E}{V}. \tag{20}$$

Now it is known from familiar kinetic theory that $\frac{2}{3}E/V$ is equal to the pressure, when all of the energy of a gas is translational, and therefore for this one system we have proved that P is equal to the pressure.

Moreover, we know from thermodynamics that $-\partial E/\partial V$ at constant entropy is equal to the pressure, thus we learn that for the monatomic gas S is constant when the entropy is constant.

The Identification of P and T with Pressure and Temperature.—Let us now consider our gas, system J, and any other system, K, separated by a movable piston, thermally non-conducting. If the two systems are at the same (average) pressure, they are in equilibrium with respect to motion of the piston. An adiabatic displacement of the piston, as we have just seen, will keep the gas at constant S, but since S does not change for the one system, it does not change for the other, according to equation (5). Therefore, for any system a change at constant entropy is a change at constant S.

Again using equation (5), we write for a small variation in the position of the piston,

$$\left(\frac{\partial E_J}{\partial V}\right)_S \delta V_J + \left(\frac{\partial E_K}{\partial V}\right)_S \delta V_K = 0, \tag{21}$$

but $\delta V_J = -\delta V_K$, hence from equation (13), $P_J = P_K$. Since we have shown that P_J is the pressure the same is true of P_K. Therefore, for any system P is equal to the pressure.

It remains now to show that T is equal to the thermodynamic temperature. We may write the identity,

$$dS = \left(\frac{\partial S}{\partial V}\right)_E dV + \left(\frac{\partial S}{\partial E}\right)_V dE, \tag{22}$$

and from equations (11) and (12),

$$dS = \frac{PdV + dE}{T}. \tag{23}$$

If the system we are considering is in equilibrium with its surroundings, $PdV + dE = q$, the heat absorbed, since P is now identified with the pressure. Therefore,

$$dS = \frac{q}{T}. \tag{24}$$

Let us now perform a Carnot cycle, first moving at constant temperature, and, therefore, as we have seen, at constant T; then at constant entropy, and, therefore, at constant S; then back at constant T to the original S, and, finally, at constant S to the original T. Let q_1 and q_2 be the heats absorbed along the first and second isothermals, then by equation (24),

$$\frac{q_1}{q_2} = \frac{T_1 dS_1}{T_2 dS_2}, \tag{25}$$

but since each isothermal lies between the same two values of S, $dS_1 = -dS_2$, and,

$$-\frac{q_1}{q_2} = \frac{T_1}{T_2}. \tag{26}$$

Now from the very definition of temperature in thermodynamics, $-q_1/q_2$ is the ratio of the temperatures. Therefore, T is always proportional to the thermodynamic temperature.

We see from equation (11) that the unit of T depends on the unit of S and we may now consider that the constant in equation (10) has been so chosen that the scale of T is the same as the ordinary temperature scale. The two are now completely identified. After having done this, we see from such an equation as (24) that S is now completely identified with the entropy.

While we have shown that S, P, and T are identical with entropy, pressure, and temperature, as used in thermodynamics, these terms are used outside of thermodynamics in a larger sense which we have not attempted to reproduce. For example, one sometimes states that the pressure in a system diminishes and the temperature increases as some chemical reaction proceeds in an isolated system, but this is inconsistent with the thermodynamic statement that the properties of a system are completely determined, let us say, by the volume, the energy, and the amount of material. As we have defined P and T, they are the average pressure and temperature over infinite time, but this is exactly what is needed in thermodynamics, for every reversible process implies infinite slowness. Fur-

thermore, in any strict sense, one cannot say that the entropy of any isolated system tends toward a maximum, for the entropy is fixed by the initial conditions and does not change at all. What can be said that comes nearest to the statement of Clausius is that, if a system is regarded as composed of a number of parts, *each of which is large*, the sum of the entropies of the parts tends toward a maximum. When the maximum is reached, the system is in equilibrium with respect to these parts; but without designating such parts the very statement that the system as a whole is in equilibrium is meaningless.

Having proved that equations 11 and 12 are identical with the two primary equations of thermodynamics, the remaining thermodynamic equations may be readily obtained. In a following paper, we shall examine the actual mode of partition into regions in concrete cases, and some of the mathematical methods which may be used for the calculation of the absolute entropy.

[1] These PROCEEDINGS, **14**, 569 (1928).

[2] Since Ω is a positive integer, this definition makes $S \geqq 0$ (the third law). It also conforms with Planck's original suggestion that the entropy is proportional to the logarithm of the number of possible states. There has, however, been much difference of opinion as to the method of computing the number of possible states. We shall discuss at another time the relation between our definition and the latest definition of Planck (*Ber., Berlin. Akad.*, **26-27**, pp. 442 (1925)) as well as the fourth definition of Shrödinger (*Ber. Berlin Akad.*, **26-27**, pp. 434 (1925)).

[3] Lewis, these PROCEEDINGS, **13**, 307 (1927); **13**, 471 (1927).

A PROPOSED EXPERIMENT ON THE NATURE OF LIGHT

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It has long been known that light appears to possess a dualistic character. Many radiation phenomena, such, for example, as interference, receive a rational interpretation by assuming that light consists of electromagnetic waves obeying the Maxwellian equations. On the other side, such experiments as the photo-electric effect show clearly that in the emission or absorption of radiation by matter, the radiant energy appears to be localized in groups or bundles of the magnitude $h\nu$, a conception quite foreign to the wave picture.

A number of rather artificial attempts have been made to reconcile the existence of light quanta with the classical wave theory, but without success, and it has remained for the quantum mechanics to show that both light and matter essentially possess a dualistic character and that no self

contradiction is thereby involved. According to this view of the nature of radiation we may say that all questions relating to the mean energy (i.e., the mean number of light quanta) appearing at any point will be correctly answered by the Maxwellian equations. If, on the other hand, we are dealing with individual processes of absorption or emission we shall expect the radiation energy to exist only in discrete bundles of the magnitude $h\nu$, the actual appearance of such bundles being governed by the laws of probability.

As an example of the application of this view we may think of a ray of monochromatic light falling upon a diffraction grating. On a screen some distance away from the grating there will appear a number of spots of light corresponding to the various orders of reflection 0, $\pm$ 1, $\pm$ 2, etc., where the mean intensity of each spot may be computed in the usual manner by applying the theory of electromagnetic waves. Let us suppose that we possess a suitable means for measuring and recording quantities of radiation as small as $h\nu$ separately. We should then believe that fluctuations of this order of magnitude would be observed at each of the diffraction spots and that these fluctuations would be independent for each spot. This conclusion would present two contradictions to the predictions of the classical wave theory, first, in the existence of discrete quanta of energy and, second, in the independence of the distribution of these quanta over the diffraction spots, for in the wave theory of interference a wave-train of energy $h\nu$ falling on a grating must of necessity be simultaneously distributed over the various orders of reflection. This would however involve a splitting up of the light quantum, contrary to the results of the experiments on the photoelectric effect.

The conclusions that have just been reached concerning the behavior of light at a diffraction grating might be tested experimentally by using as a source of radiation a beam of high frequency x-rays, a crystal lattice as the grating, and a Geiger counter to measure the presence of the light quanta. The beam of x-rays should fall on a single crystal and at the positions of two Laue spots, say of equal intensity, two Geiger counters should be placed. Let the intensity of the original beam be so adjusted by means of filters that only a few light quanta would fall upon each of the counters per minute. If the classical wave theory alone governed the transmission of light, then the absorptions at the two Geiger counters must take place simultaneously since it is essential to this theory that any group of waves, however faint, arriving at a grating will be diffracted to all the orders of reflection simultaneously. If, however, the view presented at the beginning of this note is correct, we may expect that the absorptions at the two counters will be independent and governed only by the laws of probability in such a manner that the mean energy arriving at each spot will be equal to that predicted by means of the wave theory.

THE SPECTRUM OF X-RAYS FROM THE BACK OF A TUNGSTEN TARGET

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If an electron beam under the influence of the electric field between anode and cathode hits any kind of target, this target becomes a source of new electron rays which consist of real reflected (at very low voltage), rediffused, secondary and photoelectrons. The paths of these electrons will be bent backward by the positive field of the anode and, in case of a high vacuum tube, by the negative field of the glass-walls, and thus hit the anode over its whole length.

In working with an x-ray tube at rather high voltages the properties of these "reflected" electrons can be investigated by means of the radiation which they produce. Coolidge[2] first investigated this radiation and his results have been verified by other authors.[3] Coolidge found that the total amount of this radiation was about 24% of the focal spot radiation, and that, generally, it was a little softer than the radiation from the focal spot. The experiments described in this paper were performed for the purpose of studying the spectral distribution of this radiation from the back of a tungsten target, to obtain in this way some information about the electrons producing it.

Because this radiation—sometimes called "stem" radiation—is only about 24% of the focal spot radiation and, furthermore, originates from the whole length of the anode a special tube was constructed in order to get enough intensity. The anode was taken from a Coolidge standard tube, the club-shaped part of which consisted of tungsten. The cathode, with a tungsten filament, was so arranged in a side tube, figure 1, that the electrons must hit the longer part of the club. Part of the "reflected" electrons will hit the front plane of the club there producing x-radiation. This front plane was placed nearly parallel to the slit of the spectrometer. By this arrangement sufficient radiation for the measurements was obtained. The distance between anode and filament was small, 1.5 cm. to prevent primary electrons from hitting the front plane.

Extreme care was used in degassing the anode, to be sure that no disturbing effects in the emission of the "reflected" electrons from the anode might appear.[4] Besides, in working with this tube, an electron current as high as possible was used in order to have the anode white hot during the measurements, thus destroying the absorbed O_2 layer that cannot be removed at temperatures below 1500°.

The voltage applied to the tube was delivered by the 100,000 volts

storage battery of the institute. Its amount was measured by a calibrated high voltage electrometer and by determining the limit of the spectrum of the focal spot radiation. A water resistance was provided to maintain a constant voltage. A small storage battery provided the current for the filament. The spectrometer used was the ordinary Bragg spectrometer with a calcite crystal and an ionization chamber filled with methyl-iodide. A quadrant electrometer measured the ionization current. The measurements consisted in determining the intensity distribution as a function of wave-length for both the focal spot and the stem radiation.

The following voltages were used: 22,400, 36,500, 49,400, 71,600 and 82,500 volts and for each radiation the ionization currents were measured as a function of the crystal angle, the zero of which was obtained by measuring the position of the absorption limit of silver. The silver absorption limit, also, was used for determining the slit correction. Figures 2, 3, 4 represent part of the curves obtained after applying the slit correction. Figure 2 shows the spectra for both focal spot and stem radiation. The spectrum of the focal spot radiation has the usual form; the limiting wave-length is obtained by extending the straight part of the curve downward. The point of intersection with the horizontal line of zero intensity gives the limit and with it the voltage applied to the tube by the photoelectric equation. This value was checked for every measurement by the electrostatic voltmeter. Both values agree in the case of figure 2 within about 0.4%. There is some radiation beyond the limit toward shorter wave-lengths, which is chiefly due to generally scattered rays. As for the stem radiation there is no perceptible radiation from the limit of the focal spot radiation toward

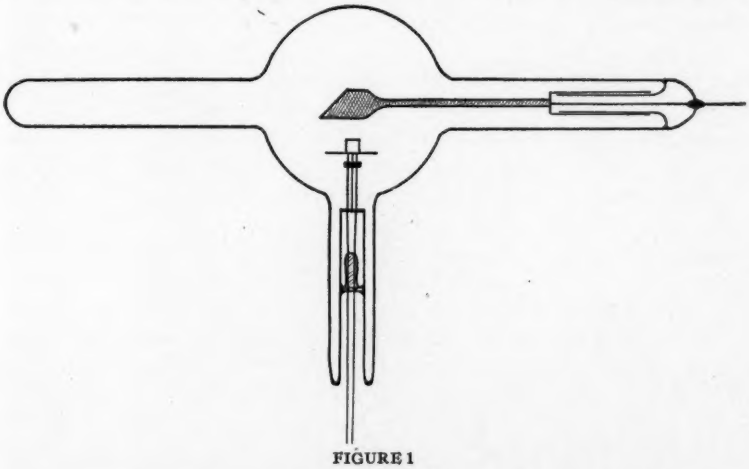

FIGURE 1

longer wave-lengths up to a crystal angle of 5°40′, at which point the spectrum of the stem radiation appears. In the same way as for the focal spot radiation the wave-length limit for the stem radiation is obtained. As a matter of fact this limit is not as sharp as that for the focal spot radiation, but this cannot be expected, because, in producing the focal spot spectrum, electrons of uniform velocity hit the target, whereas in the case of the stem radiation one has to expect electrons of different velocities on account of their origin at different depths below the surface of the anode.

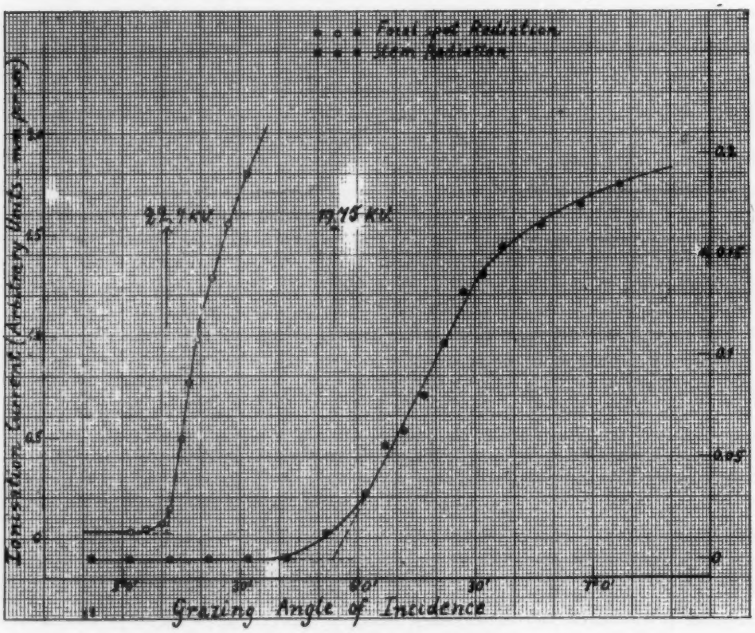

FIGURE 2

However, the fact that there exists a limit for the stem radiation shows that the "reflected" electrons have a velocity limit. In calculating the voltage of this limit the value of 19,750 volts was obtained for the highest velocity of the "reflected" electrons in the case of figure 2. That means a loss of 2650 volts.

Figures 3 and 4 give the spectra for voltages of 49,400 and 83,350 volts applied to the tube. The general course of the spectra is the same as for 22,400 volts. In every spectrum of the stem radiation a limit was found. For the stem radiation of 49,400 volts the loss of voltage for the "reflected" electrons amounts to 4500 volts and for 83,350 to 10,750 volts.

The results obtained are put together in table 1.

TABLE 1

BY ELECTROMETER	VOLTAGE FROM LIMIT OF FOCAL SPOT RADIATION	VOLTAGE FROM LIMIT OF STEM RADIATION	DIFFERENCE BETWEEN LIMITS OF FOCAL SPOT AND STEM RADIATION IN VOLTS	EXCITATION VOLTAGE (TUNGSTEN LEVELS)
22,480	22,400	19,750	2,650	590 for N_7 level
36,600	36,500	33,100	3,400	2,820 for M_5 level
49,350	49,400	44,900	4,500	12,700 for L_3 level
71,600	....	63,500	8,100	11,520 for L_2 level
82,500	83,350	72,600	10,750	10,200 for L_1 level

Column 1 of this table contains the voltages applied to the tube measured by the electrometer. Column 2 contains the voltages calculated from the shortest wave-length of the focal spot radiation; column 3, those from the

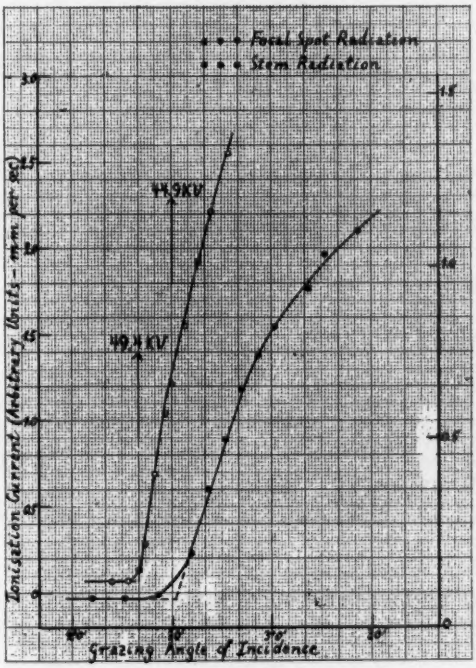

FIGURE 3

shortest wave-length of the stem radiation, whereas the voltages applied to the tube are the same as for the focal spot radiation. Column 4 gives the difference between the two values.

As is to be expected there are no real reflected electrons concerned in producing the stem radiation. Furthermore, there seems to be no possibility of explaining the shortest wave-length of the stem radiation as produced by rediffused electrons; although primary electrons may suffer some loss of velocity by the process of rediffusion.[5] This loss of velocity cannot be uni-

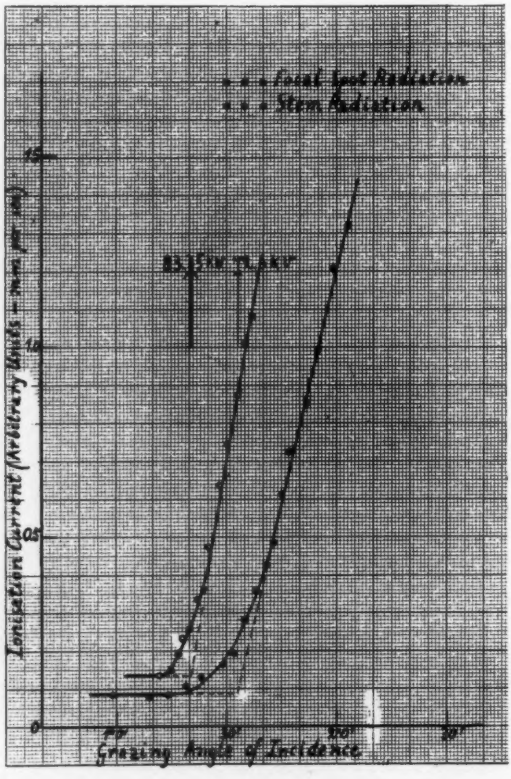

FIGURE 4

form and, therefore, it seems to be impossible to explain the well-developed limit of the spectrum of the stem radiation as produced by rediffused electrons.

Let us consider more closely the voltage corresponding to the difference of the shortest wave-lengths between focal spot and stem radiation as it appears in table 1, column 4. This difference amounts to 2650 volts for 22,400 volts and to 10,750 volts for 83,350 volts applied to the tube, and corresponds very closely to the excitation voltage of the M_5 and L_1 or L_2

levels, respectively (Table 1, Column 5). Therefore, it seems to be most likely that the "reflected" electrons in these cases consist chiefly of secondary and photoelectrons, the first removed by single impacts of primary electrons with tungsten atoms, the latter produced by absorption of general radiation by the atoms of the anode within the target. The velocity of these electrons, therefore, cannot be greater than that of the primary electrons minus the excitation voltage of the level. All smaller velocities can appear, of course. In the experiments described in this paper it is not possible to distinguish between secondary and photoelectrons but the amount of secondary electrons exceeds that of photoelectrons probably very greatly. Webster[6] has found a value for the ratio of direct to indirect ionization for silver.

It has to be explained now, why no secondary electrons from the other levels, e.g., the N levels appear in the case of 22,400 volts and neither N nor M electrons in the case of 83,350 volts across the x-ray tube. The voltage of 22,400 volts corresponds to about 40 times the excitation voltage of the N_7 level and more for the other N levels. Therefore, it has to be assumed that almost no absorption of primary electrons in any level takes place in the tungsten anode, if the energy of primary electrons exceeds that of the level by about 40 times. Thus, almost no N electrons will participate in the production of the limit of the stem radiation. As for the M electrons, the voltage of 22,400 volts is about 7 times the excitation voltage of the M_5 level, which level only will be important for the absorption of primary electrons of the velocity corresponding to 22,400 volts. It is known that the greater the energy of γ-rays, the larger is the proportion of them absorbed in higher levels of any series in comparison with that in the other levels.[7] In addition to the M electrons, L electrons will participate in the production of the stem radiation. The higher the voltage across the tube the more L electrons will appear and the fewer M electrons. It cannot be expected to distinguish between the kinds of electrons in the spectrum of the stem radiation. Due to the fact that secondary electrons of any velocity, from deeper parts of the anode, will appear in addition to the limit velocity, the x-ray spectrum, produced by these electrons must necessarily have a very flat maximum. Both spectra, that of the M and that of the L electrons will add in such a way that the spectrum shows a medium limit according as more M or more L electrons are present. Therefore, the difference of voltage increases in the measurement at 36,600 volts and still more (Table 1) at 83,350 volts, which is about 30 times the excitation voltage of the M_5 level. At this voltage, almost all M electrons have disappeared and the limit of the stem radiation is determined by the L electrons only. It was not possible to work at higher voltage because the tube (the only one of 8 that has stood the constant voltage of the battery) broke.

Summing up the results of this paper: the stem radiation of an x-ray

tube with tungsten anode seems to be produced at high voltage across the tube mostly by secondary electrons knocked out from the levels of the tungsten atom. The probability that an absorption takes place in any level is a function of the voltage applied to the tube, it reaches a maximum and decreases nearly to zero for energies of primary electrons exceeding that of the level by about 40 times. What happens for the absorption of a primary electron must happen for the emission of the characteristic quantum also, because each absorption process of an electron in any level corresponds to the emission of a characteristic ray. Therefore, we have to expect that the intensity of any characteristic series due to the knocking out of electrons of an atom must increase first and then decrease with increasing voltage across the x-ray tube.

The writer desires to thank Professor Duane for his many helpful suggestions and his valuable criticism while this investigation has been in progress.

[1] INTERNATIONAL RESEARCH FELLOW.

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[7] L. Meitner, *Ztschr. Phys.*, **34**, 810, 1925.

ABSOLUTE X-RAY WAVE-LENGTH MEASUREMENTS

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Communicated June 11, 1928

As a result of their work on the diffraction of x-rays by a ruled grating, Compton and Doan (*Proc. Nat. Acad. Sci.*, **11**, 598 (1925)) made the statement that they saw "no reason why measurements of the present type may not be made fully as precise as the absolute measurement by reflection from a crystal, in which the probable error is due chiefly to the uncertainty of the crystalline grating space." Work has been in progress with the view of getting more precise measurements by this method than is at present possible by the crystal method. The method used follows closely that of Compton and Doan, rather than that of Thibaud (*Rev. d'Op.*, **5**, 105, 1926; *Phys. Zeit.*, May, 1928, and elsewhere).

With the small glancing angles (large angles of incidence) used, the usual formula for wave-length in optical work becomes:

$$n\lambda = D\left(\alpha\theta + \frac{1}{2}\alpha^2 - \text{4th degree terms}\right)$$

where D is the grating space, n is the order of diffraction, θ is the glancing angle, α is the angle between the zero order and the nth order. It was found unnecessary to use the 4th degree terms. Very accurate determinations of α and θ are thus required for a precise determination of the wavelength.

The experimental arrangement is shown diagrammatically in figure 1. The particular line to be measured was reflected from a calcite crystal C and collinated by the slit S_2 before reaching the grating G. The grating was so aligned that the x-ray beam would be reflected first in one position, then in a position approximately 180° from it. The dotted line DG is the direct beam; $G + 0$ the reflected beam from the face of the grating as shown, called positive zero for short; the dot-dash line $G - 0$ the re-

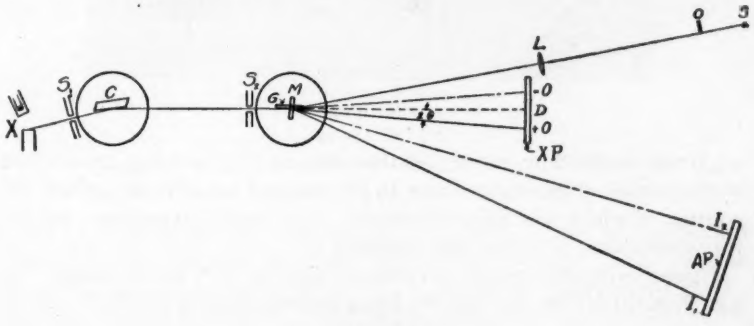

FIGURE 1

flected beam in the second position, called negative zero. In order to obviate the necessity of measuring the indeterminate distance from the plate to the effective part of the grating for the purpose of determining the glancing angle, a plane parallel mirror M was mounted on the grating table so as to move as an integral part of it and the image of a straight edge O brought to a focus on the plate AP, I_1 corresponding to $+0$, I_2 to -0. With this arrangement no negative order was necessary for determining the glancing angle.

Having aligned the apparatus photographically the following steps were taken. The grating was first moved out of the beam and a short exposure of the direct beam recorded on the plate XP. This place on the film was then protected from further immediate exposure with a strip of lead and the grating moved back to its position and a short exposure taken to record the negative zero order. The position of the grating was then recorded by an exposure on plate AP after which the grating was turned

and the positive position recorded. Sufficient time was allowed for the recording of the positive zero order on plate XP, then the direct beam was uncovered and a lead frame placed in front of the film so that only the central portion was exposed to the action of the x-rays. When the exposure had been going for a time sufficient to record several orders of the spectrum and before the plate XP was removed, a check on the glancing

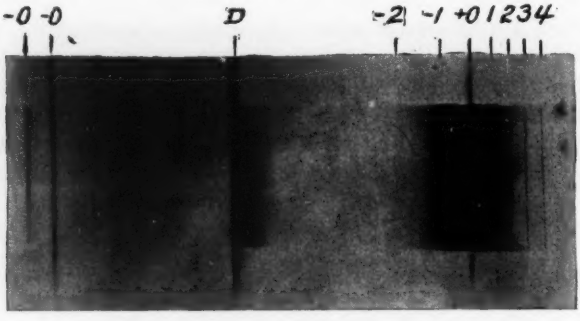

FIGURE 2

angle was obtained by putting another plate at AP, recording the position of the grating, then rotating back to get a second negative zero order, the position of which was also determined. The room temperature did not vary more than 1°C. during the exposure.

Figure 2 is an enlargement of a plate obtained at XP, and is typical. It was obtained for the $K\alpha_1$ line of Cu at a glancing angle of 21′ 19.5″ after an

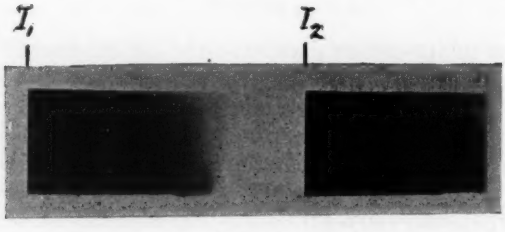

FIGURE 3

exposure of about 30 hours at a distance of approximately 1 meter. The tube was operated at about 30 kv. peak. The two negative zero orders are shown at -0, direct beam at D, positive zero order at $+0$, two negative diffracted orders at -2, and -1, and four of the six measurable positive diffracted orders at 1 to 4. The 6 positive orders are easily visible and measurable on the original negative. The broad beam beside D is that

part of the direct beam which passed the grating. Figure 3 shows the type of plate obtained at AP, the distance MI_1 being about 2 meters.

If $I_1I_2 = c$, $MI_1 = d$, $D - 0 = a$, $D + 0 = b$, $\frac{c}{d} = m$ and $\frac{a}{b} = l$ then $\tan 2\theta = \frac{m}{l+1}$, to the degree of accuracy required. Having determined θ it is an easy matter to determine $\theta + \alpha_n$ and hence α_n. Measurements of the plates XP and AP were made on two comparators on different days and results of different observers used. The only distances not measured on the comparator were MI_1 and the grating space. The former was measured by making fiducial marks on a steel tape and comparing the distance between these marks with a standard meter. The results obtained from measurements of some of the plates on hand are given below. In each case a speculum metal grating was used. Only 5 mm. were ruled, the length of the lines being 2 cm. The grating space as determined with a Geneva spectrometer using the green line of mercury was 2.0000×10^{-3} cm. The column at the right are the values taken from Siegbahn, "The Spectroscopy of X-Rays" (Ox. Univ. Press, 1925), p. 105.

Cu $K\alpha_1$	1.5374 ± 0.0006	1.53730 Å
Fe $K\alpha_1$	1.937 ± 0.004	1.93230 Å
Mo $K\alpha_1$	0.708 ± 0.002	0.70759 Å

The probable errors are those estimated from the errors in the measurements of the distances involved. The Cu wave-length is the weighted mean of measurements on the 1, 2, 3, 4, 6 positive orders of the plate of figure 2. That for Fe is the result of a calculation on only 1 positive order, and although the lines of the plate were not as sharp as on plates for Cu and Mo, the angles were of such a magnitude as to partly offset this circumstance. The Mo wave-length is the weighted mean of three measurements on first-order spectra only. The sharpness of the lines seems to warrant recording the result.

A continuation of the work is in progress. The writer wishes to thank Professor A. H. Compton for his keen interest and for the valuable suggestions he has made. Acknowledgment of the suggestions of Dr. J. A. Bearden is also made and indebtedness is due Dr. R. L. Doan who had designed a considerable part of the apparatus before the writer started work.

ON THE THERMODYNAMIC EQUILIBRIUM IN THE UNIVERSE

By F. Zwicky

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Communicated June 19, 1928

With the establishing of the second law it was realized that all the actual processes on earth are irreversible and unidirectional in the sense of this law. The same is true for the solar system as the sun is radiating energy continually in an irreversible way. Because of the same phenomenon being connected with all the stars it seemed to be justified to extrapolate and to consider the actual universe as a unique one, being far from a state of thermodynamic equilibrium and running down irrevocably toward a state of highest entropy. This seems to be the general opinion up to date.[1]

However, several attempts have been made to deduce special conclusions from the postulate of a thermodynamic equilibrium in the universe. (This postulate we denote by P.)

The relativity relation between mass and energy, phenomena connected with the evolution of the stars, and the existence of the penetrating radiation, had made it probable that mass can be converted into radiant energy. Stern,[2] therefore, applied (P) to the following reaction.

$$\text{Radiation} \rightleftarrows \text{Particles (of mass } m) \qquad (1)$$

He found that the radiation is favored by a factor $e^{mc^2/KT}$ which is of the order $e^{10^{13}/T}$ for $m = m_H$. This would mean that for possible temperatures of the universe practically all the matter would disappear into radiation. Lenz[3] then considered the reaction from another point of view, taking into account the change of volume of an Einstein universe connected with the disappearence of mass into radiation. His result is that the amounts of radiation and matter are equal. But Tolman[4] afterwards showed that Lenz's considerations cannot be justified on a more general basis. He on the contrary shows, for the case considered by Lenz, that Sterns conclusions are still approximately valid, a result which is in clashing contradiction with the actual facts.

Some other considerations related to our problem were given by R. C. Tolman[5] in a paper treating the following reaction

$$4H \rightleftarrows He$$

He showed that the ratio of the concentrations of He and H in equilibrium in the universe should then be of the order $e^{\Delta m \cdot c^2/KT}$. With $m = 0.008 \times m_H$ this is approximately $e^{10^{10}/T}$. This again seems to be in strict contradiction with the ratio of the concentrations of the two elements in the stars.

However, reasons might be advanced for the view that the conditions in the stars can hardly be considered as appropriate for testing the theory. In any case a review of the results obtained so far fails to reveal any positive confirmation of the postulate (P).

It appears however to the writer, that the basis of the problem needs to be extended if it is to conform with the actual conditions. Indeed an equilibrium involving many products all of which can react with each other cannot be treated by considering the equilibrium in regard to an insufficient number of partial reactions only. Now one of the most conspicuous features of the universe lies in the phenomenon of the agglomerations of mass, which shows regularities as perfect as might be expected if postulate (P) were realized. The surprising uniformity in the characteristics of stars of the same class (age) is a fact so fundamental that we propose to treat the equilibrium between stars and free atoms in the universe precisely as we treat that between different kinds of molecules, as for instance S, S_2, S_6, S_8 in the case of sulphur vapor. There are also agglomerations of another kind like gaseous nebulae, star clusters and galactic systems, which, in the analogue of the sulphur vapor would have to be compared with swarms of molecules. Since, however, they are not units of a definite kind as are molecules they show less uniformity. Their general characteristics, however, are sufficiently alike to justify the view that they might be considered as swarms in the strict meaning of statistical mechanics. The postulate (P) then has to be applied simultaneously to the following chain of reactions.*

$$\begin{aligned}\text{Radiation} \rightleftarrows \text{Protons Electrons} \rightleftarrows \text{Higher nuclei} \rightleftarrows \\ \rightleftarrows \text{Dust Particles of all sizes} \rightleftarrows \text{Gaseous Nebulae} \rightleftarrows \\ \rightleftarrows \text{Stars} \rightleftarrows \text{Swarms of stars (Galactic systems)}\end{aligned} \qquad (1)$$

Let us first consider the following process

$$\nu \text{ atoms} \rightleftarrows \text{one star} \qquad (2)$$

A rough preliminary estimate as to the equilibrium concentration may be obtained in the following way. Let us consider stars of a certain size only and use the data known for the sun

$$M = 2 \times 10^{33} \text{ gr.} \qquad R = 7 \times 10^{10} \text{ cm.} \qquad f = 6.68 \times 10^{-8}$$

we obtain a gravitational potential energy approximately equal to

$$\Omega = -f\frac{M^2}{R} = -3.81 \times 10^{48} \text{ ergs.}$$

Assuming an average atomic weight of 50 for the particles constituting the star we obtain for the number of atoms in the star $\nu = 2.1 \times 10^{55}$.

This means that the average potential energy of one atom in the star amounts to

$$\Omega/\nu = 1.8 \times 10^{-7} \text{ ergs.}$$

The average kinetic energy of approximately $kT = 1.37\ 10^{-16}\ T$ ergs will actually always be small compared with Ω/ν (even for $T = 10^7$ degrees). As a first approximation we, therefore, may consider all the degrees of freedom in our star frozen in. Then we make use of the statistical treatment of a chemical reaction in the form given by Ehrenfest and Trkal.[6] ν_i of the molecules A_i are entering the reaction

$$\sum \nu_i A_i = 0.$$

The equilibrium constant is expressed as follows (with concentrations in numbers of molecules per cm.[3])

$$lnK_c = -\frac{1}{KT}\sum \nu_i \epsilon_i + \sum \nu_i \frac{f_i}{2} lnKT + \sum \nu_i ln a_i. \qquad (3)$$

ϵ_i is the potential energy of a molecule of the ith kind. f_i represents the number of fully excited degrees of freedom in this molecule. a_i is the chemical constant with respect to the molecule i. For monoatomic molecules it would be $a_i = (2\pi m_i)^{3/2}/h^3$. It can easily be seen that in our case only the first term on the right side of (3) is of importance. We have A_1 = atom, A_2 = star, $\nu_1 = \nu$, $\nu_2 = -1$. $\epsilon_1 = 0$, $\epsilon_2 = \Omega$. Therefore,

$$-\frac{1}{KT}\sum \nu_i \epsilon_i = \frac{\Omega}{KT} = -2.8 \times 10^{64}/T.$$

The second and the third term of (3) are of the same order of magnitude as $\nu = 2 \times 10^{55}$. They can therefore be neglected as compared with the first term, at least for all possible equilibrium temperatures of the universe. We have then essentially

$$lnK_c = ln\left(\frac{N_1}{V}\right)^{\nu}\left(\frac{N_2}{V}\right)^{-1} = -2.8 \times 10^{64}/T$$

where N_1 and N_2 are the total number of free atoms and of stars, respectively, in the universe. (V is the volume of the universe.) Denote the total number of atoms with N, then

$$N = N_1 + \nu N_2$$

Introducing the following concentrations $n = \frac{N}{V}$, $n_1 = \frac{N_1}{V}$, $n_2 = \frac{N_2}{V}$.

Making use of the ratio

$$x = n_1/n$$

our relation will be

$$x^{\nu}n^{\nu} = \frac{(1-x)n}{\nu} e^{-2.8 \times 10^{44}/T}$$

$$x^{\nu} = (1-x)e^{-2.8 \times 10^{44}/T - ln\,\nu - \nu ln\,n}.$$

To determine n we make use of the mean values for the density of matter in the universe as estimated by Hubble, $\rho = 1.5 \times 10^{-31}$ gr./cm.^{3} This leads to $n = \frac{\rho}{m} = 1.6 \times 10^{-9}$. Therefore, we have only to consider the first term in the exponential and we obtain as an order of magnitude

$$x = e^{-2.8 \times 10^{44}/T\nu} = e^{-1.3 \times 10^{9}/T}. \qquad (4)$$

The vapor pressure in the interstellar space, therefore, is extremely small. The practical limits for the size of stars, on the other hand, are given as follows. According to the accepted views the upper limit is determined by the instability of larger agglomerations. For decreasing mass the probability according to (4) is decreasing so rapidly that practically only stars near to the possible upper limit will be formed. The statistical treatment on the basis of postulate (P) therefore accounts readily for the two fundamental facts of relative emptiness of space and the existence of stars of a certain size only.

The high temperatures of the stars are not necessarily in contradiction with a much lower average temperature of the universe, as the formation of highly probable reaction products involves always excessively large kinetic energies for the individuals in the transition state.

In regard to the translational velocities of the stars it should be mentioned that they have nothing to do with the immensely small velocities corresponding to $\frac{3}{2}kT$. They are really determined by the mutual interaction of the masses. The fundamental difference of the "gas" made up by the stars and a usual "van der Waal's gas," however, lies in the fact that for the first no equation of state in the ordinary sense can exist because of the slow fading of the mass attraction with distance. The star gas might be compared with a space charge made up by ions of one sign only in which case it is known that correct results can be obtained only by considering the system as a whole.

The statistical treatment given above corresponds to an application of Berthelot's principle to a chemical reaction. It would be easy to improve this procedure by introducing the free energy instead of operating with the energy or heat of reaction. It can be shown that the value for x would be multiplied by a factor $(v)^{c\nu}$ where v is the volume of the star and c is a number of the order 1 to 10. Also one would have to take into account the actual distribution of gravitational potential energy and of kinetic

energy over the star. All these factors tend to increase the concentration x of free atoms in space, but still leave it quite small.

The question of the existence of dust particles can be treated as an evaporation equilibrium. Assuming that all the matter in the universe exists either in the form of free atoms or of dust, the vapor pressure equation shows that for temperatures below 1000° dust would exist in a considerable relative amount. This argument, however, is fallacious when applied to actual conditions. Considering the following reactions simultaneously

$$\nu_1 \text{ atoms} \rightleftarrows \nu_2 \text{ dust particles} \rightleftarrows \text{star}$$

it can be seen immediately that the possibility of stars decreases the total amount of matter in the form of atoms and dust by a very large factor. This means then that the remaining solid phase has to evaporate entirely. From this argument it can be seen how necessary it is not to consider partial equilibria only but to treat the interchange between all the possible reaction products simultaneously. Matter then in the universe, according to the above, should exist either in the gaseous form or else concentrated in stars only. This of course cannot mean that local conditions like the vicinity of stars cannot make the existence of dust particles more probable (dark clouds in interstellar space?).

In relation to the reaction (2) it should be said that it might be necessary to modify it in the following way.

$$\nu \text{ atoms} \rightleftarrows \text{one star} + \nu^1 \text{ atoms (as radiation)}$$

because of the fact that the final product star does not contain the same number of atoms it started with. The correct treatment of the above reaction might also remove Stern's difficulty. It seems to the writer that there must be involved a serious inconsistency in the present statistical treatment of radiation and matter. In Stern's result radiation seems to enter like a state of matter of high negative potential energy. In the usual considerations of equilibria between different forms of matter, however, radiation like kinetic energy represents a state of positive potential energy. Indeed, it does not matter whether the heat of reaction is liberated in the form of radiation or if it causes an increase in kinetic energy.

We then arrive at the following conclusions: (*a*) Postulate (*P*) is not justified by the facts as far as the distribution of radiation in the universe and the equilibrium between matter and radiation is concerned. It is desirable however to reconsider the problem on a broader basis as suggested in this paper.

(*b*) A consistent statistical treatment of the equilibrium of different forms of matter in the universe on the basis of postulate (*P*) promises to furnish results in agreement with the facts, as has been shown above.

* Evidence for the second partial reaction going on from left to right has been obtained recently by Millikan and Cameron. As the intensity of the cosmic radiation is of the same order of magnitude as the total intensity of star light, the building up process of matter from simple nuclei seems to go on at the same rate as the burning up of matter in the stars.

[1] See, for instance, Jeans, *Nature*, April 28, 1928.

[2] O. Stern, *Zeitschr. Elektrochemie*, **31**, 448, 1925. R. C. Tolman, these PROCEEDINGS, **12**, 670, 1926.

[3] Lenz, *Physik. Zeitschr.*, **27**, 642, 1925.

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[6] Ehrenfest and Trkal, *Proc. Amst. Acad.*, **23**, 162, 1920.

ALGAL DEPOSITS OF UNKAR PROTEROZOIC AGE IN THE GRAND CANYON, ARIZONA

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U. S. GEOLOGICAL SURVEY

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The Algonkian Proterozoic of the Grand Canyon consists of two groups of sedimentary formations about 12,000 feet in aggregate thickness, and collectively separated by one or more periods of mountain building and profound erosional effacement both from the underlying Archean Vishnu schist and the overlying Cambrian of the Paleozoic. The upper group, the Chuar, composed mainly of shales, sandstones and thin limestones, bluish, greenish gray or red, and aggregating 5120 feet, was found by Walcott to contain "a Stromatopora-like form," later described as *Collenia*, and, in the upper division, several obscure organic traces, one of which, first characterized as Discinoid, was subsequently designated as *Chuaria*.

The lower group, the Unkar, over 5500 feet thick, separated from the Chuar by a minor unconformity, embraces sandstones and shales, mainly red or purple in color, with a relatively small proportion of limestone. No traces of life have heretofore been recognized in the Unkar group. On the basis of the general characters of these two Proterozoic groups and the diastrophic evidence, Van Hise suggested the tentative correlative reference of the Unkar, which is rather heavily charged with iron, to the Lower Huronian, notwithstanding its relatively slight metamorphism on account of which he called attention to this group as a most promising series of sediments in which to search for traces of life in this ancient period.

As the result of downfaulting of masses of sediments into the Archean schist, portions of several blocks of Unkar escaped complete pre-Cambrian erosion and now lie almost entirely below the level of the Tonto platform at or near the mouth of Bright Angel Creek.

Immediately above the heterogeneous boulder bed forming the base of the Unkar follow bluish and white limestones and dolomites, generally crystalline and chert-bearing, interspersed with thin shales and banded and mottled with red or purple, in all about 300 feet, which compose the Bass limestone. On the Bass limestone rests the Hakatai shale, about 600 feet thick, composed of alternating sandy shales and quartzites overwhelmingly hematite red, and strikingly suggestive of the "Penokee" (Animikie) of the Lake Superior region. This is followed by the Shinumo quartzite, mostly quartzite and sandstones, purple and subordinately green or white, 1564 feet thick where measured by Noble in the Shinumo quadrangle. Sandstones, red, gray and greenish, about 2500 feet in thickness, form the upper part of the Unkar, the more complete section of which is found only in the eastern area studied by Walcott.

Reefs unmistakably of algal deposition and several other types of deposit very probably of algal origin were found by the writer at different levels in the Bass limestone in Bright Angel Canyon, in May, 1927, and molds fucoidal in aspect and possibly of animal but surely of organic origin, were found at about the same time by G. E. Sturdevant in the lower part of the Hakatai shale.

Four distinct forms of deposit of organic origin are recognized in the Bass limestone, besides two or three more problematic types. The first form comprises upward-arched, concentrically placed and successively overreaching, irregular concavo-convex lenses piled so as to compose very large, round-topped, biscuit-like growths, similar in many respects, at least, to the form collected by Walcott from the Chuar group and referred by him to *Collenia*. Algal deposits of comparable form and superficial structure are being laid down in some of the lime-charged streams of the Appalachian Valley at the present time.

A second type of deposit is built up in thin tabular layers increasing in size and separated by thin layers of rock of different color and texture. The organic layers are successively rolled downward at the overlapping edges. These reefs are of greater horizontal extent than those of the first type, which may be only four or five feet in greatest diameter. Additional specimens of the second or tabular form were gathered by F. E. Wright and Mr. Sturdevant in the autumn of 1927.

A third type of growth embraces small lenticular cherty bodies, about 2 to 5 centimeters in diameter and one to two centimeters thick, weathering in the form of rosettes of rather rough concentric zones of variable thickness, and darker and more ferruginous than the surrounding matrix.

The fourth type forms irregular winding and branching knobby masses, lenticular in cross-section and of slightly nodular aspect, weathering a pale greenish blue in a surrounding reddish coarse-grained limestone. The blue rock shows an irregularly concentric zonal structure, in general aspect

slightly suggestive of some of the material referred by authors to *Girvanella*.

Another type of deposit, probably of algal origin, consists of thin scales, ungulate in size, form and aspect, scattered flatwise in certain layers but not always parallel to the bedding. They weather white or very light-gray, in contrast with the darker, bluish matrix, and resemble some of the scale growths produced by modern calcareous algæ. No definite traces of organic structure have yet been noted in this type, the upper surface of which has the velvety aspect of the deposits of the scale-forming coralline.

Still another form of deposit, of chalcedonic aspect and weathering strongly in contrast with the matrix, comprises thin irregular vertical plates, 2 to 3 millimeters thick, winding and coalescing in very irregular polygonal meshes. These appear to be marked by vertical pores, somewhat variably and distantly spaced in two rows, each a little within the border. The nature of this type, which has not been studied under the microscope, is highly uncertain. It may be animal rather than vegetable or it may even be mere crack-filling, though the pattern does not appear to conform to any system of normal shrinkage or cleavage.

A form closely related to if not generically identical with Walcott's *Chuaria*, from the Chuar, also is present. It may be of plant origin, and can hardly be a bivalve.

Traces of alga tubes, and cavities similar to those in some of the reef heads formed by blue-green algæ at the present day are more or less obscurely visible in the first, third and fourth of the enumerated types. Some are visible under very low powers. They lie in oblique as well as vertical and horizontal positions. Branching is distinct in some cases. The walls of lime deposited about the living algæ were generally of smaller crystals, less strongly knit, and now in many cases appear lighter in color than the coarse interlocked calcitic crystals which fill the cavities and intervening spaces. The original tube walls are however weaker in some cases, and fractures tend to follow them, thus making their detection easier under the hand lens. Evidently most of the original matter has been obliterated by recrystallization; magnification only emphasizes crystal details, and it remains to be seen whether any minute features of the algal thalli may be detected by selective etching, or by the discovery of material better preserving the forms of the plant parts.

The material noted above but not yet fully studied was discovered in the course of the search for data relating to the conditions of deposition, the life and the history of the older formations in the Grand Canyon, and, in particular, in the preparation of exhibits of the remains of life *in situ* in locations visible from the scientific observation station on Yavapai Point. The research was carried out mainly under a grant from the Carnegie Institution of Washington, and was conducted in coöperation with the work of the National Academy of Sciences on the development of the inspira-

tional and educational resources of the Grand Canyon. The research and investigation conducted under the auspices of the Academy is supported by a grant from the Carnegie Corporation of New York.

The fossil remains discovered in the Unkar are the oldest yet brought to light in the southwest and, notwithstanding the fortunately relatively slight degree of metamorphism of the sediments, may be as old as the lower Huronian. On the other hand, they may not be older than the Keweenawan.

It is probable that some at least of the types of organic deposits in the Unkar which are shown to have been laid down in very shallow waters disturbed by winds and currents, sometimes beneath rainy skies, sometimes under a hot sun, are due to algæ of the blue-green family, the Cyanophyceæ. The abundance and indicated variety of forms of deposit, some of which may be of animal origin point encouragingly to the possibility of greatly adding to our knowledge of the certainly highly differentiated late Proterozoic life, which may have had its beginnings as long in advance of the Paleozoic as from the beginning of the Paleozoic to the present. They also give promise of paleontological criteria characteristic of the different groups of sedimentary rocks and far more valuable for the time classification and correlation of the not too far altered pre-Cambrian formations than any means now available.

ERRATA TO THE NOTE: "On Some Properties of One-Valued Transformations of Manifolds," these PROCEEDINGS, **14**, 206–214, 1928.

P. 208, lines 1, 2, 5, 7, read p instead of π; p. 209, line 8, read $|A_\nu|$ instead of A_ν; p. 211, lines 20, 21, read ϵ instead of e; p. 211, last line, the homology should be numbered (13b); p. 212, line 9, read β instead of B; p. 214, line 10, read J. instead of Y.: p. 214, line 12, read 71.1 instead of 1.1.